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JOURNAL

OF

THE CHEMICAL SOCIETY.

TRANSACTIONS.

I.—*Chemical Examination of the Root of Ipomoea orizabensis.*

By Frederick Belding Power and Harold Rogerson.

The root of *Ipomoea orizabensis*, Ledanois (Nat Ord. *Convolvulaceae*) has attracted considerable attention in recent years on account of having been brought into commerce under the name of "Mexican Scammony Root," and the fact that the resin prepared therefrom has displaced to a considerable extent the true scammony resin (from *Convulvulus Scammonia*, Linné), the two products having been generally considered to be chemically identical.

The root under consideration has been described in the "Pharmacographia," 2nd edit., p. 446, and more recently by Mr. E. M. Holmes (*Pharm. J.*, 1904, **72**, 326). It is known under various names besides that above mentioned, such as "Light, Fusiform, or Woody Jalap," "Orizaba Root," and to the Mexicans as *Purgo macho.*

The resin obtained from the above-mentioned root, which is usually stated to be completely, or almost completely, soluble in ether, has been the subject of several more or less extended investigations (compare van Ryn, "Die Glykoside," p. 396, and Tschirch, "Die Harze," Bd. II., p. 886). Among the earliest of these investigations may be mentioned those of Johnston (*Phil. Trans.*, 1840, Part II., p. 342), Kayser (*Annalen*, 1844, **51**, 101), and Mayer

(*Annalen*, 1855, **95**, 129), the last-mentioned author having given to the resin from *Ipomoea orizabensis* the name "jalapin"* ("jalappin"), whilst the resin of jalap, or the portion of the latter insoluble in ether, was designated "convolvulin." To the so-called "jalapin," the glucosidic character of which was recognised, Mayer assigned the formula $C_{34}H_{56}O_{16}$. He stated that by the action of alkalis it is converted into "jalapic acid," $C_{34}H_{60}O_{18}$, a yellow, amorphous mass, which is readily soluble in water or alcohol, and that on heating either jalapin or jalapic acid with dilute acids they are resolved into sugar and "jalapinol" or "jalapinolic acid," the latter having been given the formula $C_{16}H_{30}O_3$.

Spirgatis (*Annalen*, 1860, **116**, 289), as also Poleck (*Chem. Centr.*, 1892, II., p. 786), believed to have proved the identity of jalapin with the resin of scammony or "scammonin," and this was subsequently affirmed by Kromer (*Chem. Centr.*, 1895, II., pp. 228, 449, 495). The last-mentioned investigator, who has most recently assigned to jalapin the formula $C_{49}H_{90}O_{23}$, or

$$C_{34}H_{63}(C_5H_9O)_3O_{20}$$

(*Arch. Pharm.*, 1901, **239**, 388), showed that by the action of alkalis on the convolvulaceous resins, not only the respective "glucoside acids" are produced, but also volatile acids, as well as acidic substances which are soluble in ether and not volatile in steam; thus the jalapin from *Ipomoea orizabensis*, on treatment with barium hydroxide, was stated (*loc. cit.*, p. 373) to yield, besides the so-called jalapic acid, α-methylbutyric and tiglic acids, together with a tetrahydroxydecylic acid, $C_{10}H_{20}O_6$.

The previously-mentioned jalapinolic acid, which crystallises in small, colourless needles, was made the subject of a special investigation by Kromer (*J. pr. Chem.*, 1898, [ii], **57**, 448). He found it to melt at 67—68°, and to possess the formula $C_{16}H_{32}O_3$, also stating it to be optically inactive. Several derivatives of the acid were prepared, and, having thus ascertained that it was not identical with α-hydroxypalmitic acid, it was considered, in view of its chemical behaviour, to be represented by the formula

$$CHMeEt\cdot CH(OH)\cdot [CH_2]_{10}\cdot CO_2H.$$

Notwithstanding the number of investigations relating to the so-called "jalapin," as indicated by the brief survey of the literature given above, it has appeared to us that a more complete examination of this product was desirable, especially as the statements concerning its composition and chemical characters are so confused and divergent. With consideration of the facts already known, it is obvious that the resin in question cannot be regarded as a definite compound, or represented by any one of the numerous formulæ hitherto assigned to it. As the present authors have recently shown (*J. Amer. Chem. Soc.*, 1910, **32**, 80) that the true jalap resin (from *Ipomoea Purga*, Hayne), commonly designated "convolvulin," does not consist of a single definite glucoside, but is an exceedingly complex mixture, the constituents of which are not entirely glucosidic, it was thought probable that the same conditions would exist with regard to other convolvulaceous resins, and the correctness of this conclusion has now been rendered evident.

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* The term "jalapin" was originally applied to the chief portion of jalap resin, which is insoluble in ether, and it appears still to retain this meaning in England, but in order to avoid further confusion the name is employed in this communication in the sense denoted by Mayer.

Although the primary object of the present investigation of "Mexican Scammony Root" was to determine more exactly the chemical characters of the resin prepared therefrom, consideration has also been taken of its other constituents.

EXPERIMENTAL.

The material employed for this investigation consisted of a bale of the so-called "Mexican Scammony Root," which conformed in its characters to the recorded description (*loc. cit.*) of the root of *Ipomoea orizabensis*, Ledanois, and its authenticity was kindly confirmed by Mr. E. M. Holmes, F.L.S.

As a preliminary experiment, 50 grams of the ground material were successively extracted in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried at 100°, were obtained:

Petroleum (b. p. 40—60°)	extracted	0·55	gram	=	1·10	per cent.
Ether	,,	4·92	,,	=	9·84	,,
Chloroform	,,	0·48	,,	=	0·96	,,
Alcohol	,,	5·09	,,	=	10·18	,,
	Total	11·04	grams	=	22·08	per cent.

Determination of the Total Resin.—Fifty grams of the ground root were completely extracted with hot alcohol in a Soxhlet apparatus. To the liquid thus obtained, 25 c.c. of water were added, the alcohol then evaporated, and the separated resin thoroughly washed with hot water, after which it was dried in a water-oven until of constant weight. The mean of two nearly concordant determinations was an amount equivalent to 14·55 per cent. of resin in the root. The proportion of this crude resin which was soluble in ether, as determined by its complete extraction in a Soxhlet apparatus, was equivalent to 71 per cent. of its weight.

Extraction of the Root with Alcohol.

For the purpose of a complete examination of the constituents of the root, a quantity (48·76 kilograms) of the ground material was extracted by continuous percolation with hot alcohol. After the removal of the greater portion of the alcohol, 15·59 kilograms of a soft, dark-coloured extract were obtained.

Isolation of Sucrose.

Inasmuch as it has been shown by Requier (*J. Pharm. Chim.*, 1905, [vi], **22**, 435, 492) that scammony root contains sucrose as well as reducing sugar, it was deemed desirable to ascertain whether sucrose is also contained in the root of *Ipomoea orizabensis.* For this purpose about 1 kilogram of the above-mentioned alcoholic extract was mixed with water to separate the resin, the dark-coloured aqueous liquid filtered, and treated with an excess of milk of lime. The mixture was then filtered, the alkaline filtrate saturated with carbon dioxide, again filtered, and the clear liquid evaporated under diminished pressure to the consistency of a syrup. By treating the latter with successive portions of alcohol, a product was finally obtained, which was completely soluble in 85—90 per cent. alcohol, and, after inoculation with a trace of sucrose and keeping for a few days, deposited a small amount (0·3 gram) of a substance in colourless prisms. After recrystallisation from slightly diluted alcohol, the substance melted at 184—185°, as did also a specimen of pure sucrose when heated somewhat rapidly, although the melting point of the latter is usually stated to be 160°. The general properties and an analysis of the substance definitely established its identity as sucrose. (Found, $C=42·1$; $H=6·8$. Calc., $C=42·1$; $H=6·4$ per cent.)

Distillation of the Extract with Steam. Separation of an Essential Oil.

A quantity (2 kilograms) of the above-mentioned extract was mixed with water, and distilled in a current of steam. The distillate, which contained some oily drops floating on the surface, was extracted with ether, the ethereal liquid being dried and the solvent removed, when a small amount (0·9 gram) of a pale yellow essential oil was obtained. This possessed a persistent odour, and gave the colour reaction for furfuraldehyde.

After the above-described operation, there remained in the distillation flask a dark-coloured aqueous liquid (A) and a quantity of a soft resin (B). The resin was repeatedly washed with hot water until the latter remained colourless, and the washings added to the main portion of the aqueous liquid.

Examination of the Aqueous Liquid (A).

Isolation of Scopoletin, $(CH_3{\cdot}O)(OH)C_6H_2{\cdot}CH{:}CH{\cdot}CO{\cdot}O$.

The aqueous liquid was concentrated under diminished pressure to the volume of about 5 litres, and repeatedly extracted with ether. The ethereal liquid was then shaken successively with aqueous ammonium carbonate and sodium carbonate, and finally with a 10 per cent. solution of sodium hydroxide. Only a small amount of a fluorescent substance was removed by this treatment, and on subsequently drying and evaporating the ethereal liquid nothing remained. The original aqueous liquid was then extracted repeatedly with chloroform, and the chloroform extracts shaken with aqueous sodium carbonate, when a further quantity of the fluorescent substance was removed. The sodium carbonate extracts from both the ethereal and chloroformic liquids were united, acidified, and shaken with chloroform, when, after drying and evaporating the solvent, a quantity (0·9 gram) of a crystalline substance was obtained. On recrystallisation from absolute alcohol, it separated in pale yellow needles, which melted at 203—204°, and gave with alkalis a brilliant, blue fluorescence. (Found, $C=62{\cdot}6$; $H=4{\cdot}3$. Calc., $C=62{\cdot}5$; $H=4{\cdot}2$ per cent.)

An acetyl derivative, prepared by heating the substance with acetic anhydride, separated from absolute alcohol in slender, colourless needles, melting at 177°. The substance was thus identified as scopoletin (4-hydroxy-5-methoxycoumarin), which has previously been obtained from several plants (compare Trans., 1911, **99**, 1043).

The original aqueous liquid, which had been extracted with both ether and chloroform as above described, was next shaken with successive portions of amyl alcohol, these amyl alcoholic liquids being then united, washed with water, and concentrated under diminished pressure. A dark-coloured, syrupy product was thus obtained, which was almost insoluble in cold, but completely soluble in hot, water.

Isolation of 3 : 4-*Dihydroxycinnamic Acid*, $C_6H_3(OH)_2{\cdot}CH{:}CH{\cdot}CO_2H$.

The above-mentioned syrupy product was heated for a few minutes with a 10 per cent. solution of potassium hydroxide, the liquid then cooled, acidified, and extracted with ether. The ethereal liquid was afterwards shaken with four successive portions of aqueous ammonium carbonate, and the alkaline liquids separately acidified, when crystalline precipitates were produced. On subsequently extracting the ethereal liquid with solutions of sodium carbonate and sodium hydroxide, only amorphous products were obtained, and on finally evaporating the ether, nothing remained. The above-mentioned crystalline precipitates were found to be identical, and the whole was therefore recrystallised from hot water containing a little alcohol. The substance was thus obtained in pale yellow, prismatic needles, which melted and decomposed at 223—225° with evolution of gas, and this melting point was not changed by further crystallisation. The total amount of substance was 12 grams. In aqueous solution it gave a dark green colour with ferric chloride. After drying at 110°, it was analysed. (Found, $C = 60{\cdot}2$; $H = 4{\cdot}7$. Calc., $C = 60{\cdot}0$; $H = 4{\cdot}4$ per cent.)

The substance thus appeared to be 3:4-dihydroxycinnamic acid (caffeic acid), the melting point of which, however, has been variously recorded as 185°, 209°, and 213°.

In order further to confirm the identity of the acid, a portion of it was methylated by means of methyl sulphate, and the product recrystallised from absolute alcohol. It separated in needles melting at 180—181°, and this melting point was not altered when mixed with pure 3:4-dimethoxycinnamic acid (Trans., 1910, **97**, 1946).

Another portion of the acid was acetylated by boiling with acetic anhydride. On crystallising the product from dilute alcohol, the diacetyl derivative separated in needles melting at 198°, the melting point of this compound having previously been recorded as 190—191° (*Ber.*, 1878, **11**, 657).

Methyl 3:4-*Dihydroxycinnamate*, $C_6H_3(OH)_2\cdot CH\colon CH\cdot CO_2\cdot CH_3$.—As this compound appears not to have previously been prepared, a small quantity of the respective acid was dissolved in methyl alcohol, and the solution saturated with dry hydrogen chloride. The product of the reaction was poured into water, and the mixture extracted with ether, the ethereal liquid being washed with water and aqueous sodium carbonate, dried, and the solvent removed. A substance was thus obtained, which, when recrystallised from dilute alcohol, separated in pale yellow needles, melting at 158—160°:

0·1744 gave 0·3962 CO_2 and 0·0846 H_2O. $C = 61{\cdot}9$; $H = 5{\cdot}4$.

$C_{10}H_{10}O_4$ requires $C = 61{\cdot}8$; $H = 5{\cdot}2$ per cent.

The original aqueous liquid, which had been extracted with amyl alcohol as above described, was heated in a current of steam in order to expel the last traces of the alcohol, and to the warm liquid a slight excess of a solution of basic lead acetate was added, when a copious, yellow precipitate was produced. This precipitate was collected, washed, and then suspended in water, and decomposed by hydrogen sulphide. On filtering the mixture, and concentrating the filtrate, a dark brown liquid was obtained, which gave a green colour with ferric chloride, but did not precipitate gelatin. After treating the liquid with a solution of potassium hydroxide, as previously described, a further small quantity of 3:4-dihydroxycinnamic acid was obtained.

The filtrate from the precipitate produced by basic lead acetate was treated with hydrogen sulphide for the removal of the excess of lead, the mixture again filtered, and the filtrate concentrated under diminished pressure to the consistency of a syrup, which, on cooling, formed a viscid jelly. The syrup instantly reduced Fehling's solution on heating, and yielded *d*-phenylglucosazone, melting at 205—206°. In order further to confirm the identity of the sugar, a portion of the syrup was heated with acetic anhydride in the presence of a little *d*-camphorsulphonic acid. A crystalline acetyl derivative was thus obtained, which melted at 130—131°, and was identified as β-penta-acetyldextrose. Inasmuch as the original alcoholic extract has been shown to contain a small amount of sucrose, which would doubtless have become inverted during the subsequent operations of heating, it is probable that the above-mentioned syrup, in addition to dextrose, also contained some lævulose. There was, however, no evidence of the presence of a methylpentose.

A portion (50 grams) of the above-mentioned syrup was heated with 5 per cent. sulphuric acid, and the liquid extracted with chloroform, when a very small amount (0·1 gram) of scopoletin was obtained, thus indicating the presence of a glucoside of this substance. The attempts which were made to isolate a glucoside from the syrup were, however, unsuccessful.

Examination of the Resin (B).

The crude resin, which had been separated from the aqueous liquid (A) as previously described, formed a dark brown mass, which, when dry, could be reduced to a light brown powder, and when treated with a little animal charcoal was obtained nearly colourless. After drying in a vacuum over sulphuric acid, it melted at 125—130°.

Optical Rotation of the Crude Resin.

Since the optical rotatory power of the various convolvulaceous resins has been considered to be a factor of some value in determining their identity and purity (compare Guigues, *Chem. Zentr.*, 1907, I., p. 309; also Power and Rogerson, *Amer. J. Pharm.*, 1908, **80**, 251, and *J. Amer. Chem. Soc.*, 1910, **32**, 85), it was deemed of interest to ascertain the optical rotation of the resin under investigation. For this purpose a portion of the resin obtained by the previously mentioned assay of the root was first employed. It was dissolved in absolute alcohol, and the solution heated with successive small portions of animal charcoal until nearly deprived of colour. The initial rotation of this solution in a 1-dcm. tube was −1°51′, and since the amount of resin in 5 c.c. of the liquid was 0·4022 gram, therefore $[\alpha]_D = -23{\cdot}0^{\circ}$. Another determination was made, with the use of a little of the above-described resin (B), which gave the following result:

A solution in absolute alcohol, of which 5 c.c. contained 0·2386 gram of resin, gave $[\alpha]_D$ −1°6′ in a 1-dcm. tube, whence $[\alpha]_D$ −23·05°.

Guigues (*loc. cit.*) considers the specific rotation of the resin from *Ipomoea orizabensis* to be within the limits of −23·5° and −25°, and Kromer (*Chem. Centr.*, 1895, II., p. 228) has observed for purified "jalapin" the values −22·84° to −23·83°. The resin of scammony root, which, as previously noted, has been considered to be identical with "jalapin" (from *Ipomoea orizabensis*), has been stated by Guigues (*Bull. Soc. chim.*, 1908, [iv], **3**, 872) to have an optical rotation varying from −18·5° to −23·5° (Kromer, *loc. cit.*, states −23·06°), whilst the resin extracted from the gum-resin scammony has a maximum value of −24·5°. Goris and Fluteaux (*Bull. Sci. Pharmacol.*, 1910, **17**, 15) have observed for the last-mentioned product a specific rotation of −24°26′.

Preliminary Extraction of the Crude Resin with Different Solvents.

In order to ascertain the general characters of the crude resin, a small portion (10 grams) of it was dissolved in alcohol, mixed with purified sawdust, and the thoroughly dried mixture extracted successively in a Soxhlet apparatus with various solvents. The amounts of extract, dried at 100°, were as follows:

Petroleum (b. p. 40—60°)	extracted	6·2	per cent.
Ether	,,	64·8	,,
Chloroform	,,	0·6	,,
Ethyl acetate	,,	24·8	,,
Alcohol	,,	2·3	,,
	Loss	1·3	,,
		100·0	per cent.

For the purpose of a complete examination, 1142 grams of the resin were employed. This was dissolved in alcohol, mixed with purified sawdust, and the thoroughly dried mixture then successively extracted in a large Soxhlet apparatus with the above-mentioned solvents.

I.—*Petroleum Extract of the Resin.*

This extract, after the removal of the solvent, was a dark brown, soft solid, amounting to 71 grams. It was dissolved in ether, and the ethereal solution extracted successively with aqueous ammonium carbonate and potassium carbonate, which, however, removed nothing. A subsequent extraction with a solution of sodium hydroxide removed only a very small amount of fatty material, which could not be obtained crystalline, and a trace of a yellow substance which gave a bright red colour with both acids and alkalis. The ethereal liquid was then washed with a little water, dried, and the solvent removed, when a quantity of a soft solid remained. This was dissolved in alcohol, and heated for about four hours in a reflux apparatus with an excess of potassium hydroxide, after which the mixture was diluted with water, and the alcohol removed in a current of steam. The alkaline liquid was then thoroughly extracted with ether, the ethereal liquid being washed, dried, and the solvent removed, when a crystalline residue was obtained.

Isolation of Hentriacontane, $C_{31}H_{64}$, *and a Phytosterol,* $C_{27}H_{46}O$.

The above-mentioned crystalline residue was dissolved in warm alcohol, when, on cooling, a small amount of a solid was deposited, which was collected and recrystallised from ethyl acetate. Two fractions were thus obtained, the first being very small in amount and melting at 60—62°, whilst the second fraction separated in plates, melting at 133—135°. The first fraction gave the colour reaction of the phytosterols, and it was therefore heated for a short time with a little phthalic anhydride. After this treatment there was isolated from the mixture a small amount of a hydrocarbon, which separated from ethyl acetate in leaflets melting at 66—68°. This substance was evidently hentriacontane, $C_{31}H_{64}$ (m. p. 68°), and when mixed with a little of this hydrocarbon of known purity the melting point remained unchanged.

The alcoholic liquid from which the above-mentioned solid had separated was concentrated, when a further quantity (1·1 grams) of substance was deposited in the form of leaflets. This was mixed with the previously obtained fraction (0·2 gram) melting at 133—135°, and the whole recrystallised from a mixture of ethyl acetate and dilute alcohol. The substance was thus obtained in handsome, pearly leaflets, melting at 135—136°, and it gave the colour reaction of the phytosterols:

0·3192, on heating at 110°, lost 0·0153 H_2O. $H_2O=4·8$.
0·1072 * gave 0·3292 CO_2 and 0·1144 H_2O. $C=83·7$; $H=11·8$.
$C_{27}H_{46}O,H_2O$ requires $H_2O=4·5$ per cent.
$C_{27}H_{46}O$ requires $C=83·9$; $H=11·9$ per cent.

A determination of the specific rotatory power gave the following result:

0·1934,* made up to 20 c.c. with chloroform, gave α_D $-0·39'$ in a 2-dcm. tube, whence $[\alpha]_D$ $-33·6°$.

The acetyl derivative was prepared by heating a little of the substance with acetic anhydride. It separated in flat needles, melting at 122—124°.

The above-described substance was thus definitely identified as a phytosterol, and, with the exception of the slightly higher melting point of its acetate, it agrees in character with verosterol (Trans., 1910, **97**, 1951).

Isolation of Cetyl Alcohol, $C_{16}H_{34}O$.

The alcoholic mother liquors remaining from the separation of the above-described phytosterol were evaporated, and the residue distilled under diminished pressure. The distillate was collected in three fractions, which passed over respectively at 190—200°, 200—220°, and 220—300°/15 mm. The first two fractions were united and recrystallised, first from light petroleum and then from ethyl acetate. A quantity (2·5 grams) of cetyl alcohol was thus obtained, which separated in small, colourless leaflets, melting at 50—51°. (Found, $C=79·0$; $H=14·0$. Calc., $C=79·3$; $H=14·1$ per cent.)

The third of the above-mentioned fractions, which was very small in amount, was crystallised from ethyl acetate, when it separated in laminæ, melting at 55—56°. It apparently consisted of a mixture of cetyl alcohol and some higher alcohol of that series.

The alkaline liquid, from which the above-described products had been removed by extraction with ether, was acidified, and again extracted with ether. The ethereal liquid was first shaken with aqueous ammonium carbonate, which removed a small amount (1·0 gram) of the previously-described 3:4-dihydroxycinnamic acid (m. p. 222—225°). It was next extracted with a solution of sodium carbonate, which removed all of the dissolved substance. The alkaline liquid thus obtained was acidified and extracted with ether, the ethereal liquid being washed, dried, and the solvent evaporated, when a quantity of fatty acids remained.

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* Anhydrous substance.

Identification of the Fatty Acids.

The above-mentioned mixture of fatty acids was distilled under diminished pressure, when it passed over between 220° and 255°/15 mm. as a light, yellow oil, and amounted to 18 grams. The acids were first separated into liquid and solid portions by means of their lead salts.

The Liquid Acids.—These acids, when distilled under diminished pressure, passed over between 220° and 235°/15 mm. as a pale yellow oil, and amounted to 9·2 grams. An analysis and a determination of the iodine value gave the following results:

0·1830 gave 0·5160 CO_2 and 0·1862 H_2O. C = 76·9; H = 11·3.
0·5154 absorbed 0·8226 iodine. Iodine value = 159·6.
$C_{18}H_{34}O_2$ requires C = 76·6; H = 12·1 per cent. Iodine value = 90·1.
$C_{18}H_{32}O_2$ „ C = 77·1; H = 11·4 „ „ Iodine value = 181·4.

From these results it would appear that the liquid acids consisted chiefly of linolic acid, with a relatively small proportion of oleic acid. This was further confirmed by the oxidation of a portion (8 grams) of the mixture with potassium permanganate, according to the method described by Lewkowitsch (*Chemical Technology and Analysis of Oils, Fats, and Waxes*, 1904, I., p. 360). The chief product of the oxidation was tetrahydroxystearic acid, melting at 158—160°. (Found, C = 61·9; H = 10·3. Calc., C = 62·1; H = 10·3 per cent.)

The Solid Acids.—These acids, when distilled under diminished pressure, passed over between 220° and 260°/15 mm. as a light, yellow oil, which solidified on cooling to a crystalline mass, and amounted to 8 grams. The mass was recrystallised from ethyl acetate, when a product was obtained which melted at 53—55°:

0·2528 gave 0·6948 CO_2 and 0·2870 H_2O. C = 74·9; H = 12·6.
$C_{16}H_{32}O_2$ requires C = 75·0; H = 12·5 per cent.
$C_{18}H_{36}O_2$ „ C = 76·1; H = 12·7 „ „

The solid product thus appeared to consist of a mixture of palmitic and stearic acids, the former predominating.

II.—*Ethereal Extract of the Resin.*

This extract, after the removal of the solvent, was a dark resinous mass, which could easily be reduced to a light brown powder, and was stable in the air. It amounted to 725 grams.

After treatment with a little animal charcoal, the optical rotatory power of the resin was determined, with the following result:

A solution in absolute alcohol, of which 5 c.c. contained 0·2072 gram of the resin, gave α_D −0°51′ in a 1-dcm. tube, whence $[\alpha]_D$ −20·5°.

Hydrolysis of the Ethereal Extract with Barium Hydroxide.

A quantity (500 grams) of the dry ethereal extract of the resin was dissolved in alcohol, and, after the addition of a little water, a cold saturated solution of barium hydroxide was gradually added until the liquid showed an alkaline reaction. It was then kept at a temperature of 35—45°, and the alkalinity maintained by the further occasional addition of small portions of solution of barium hydroxide. This treatment was continued until the liquid gave no turbidity when mixed with water, after which it was allowed to cool, and a dark brown precipitate which had formed during the hydrolysis was separated by filtration.

Isolation of Ipuranol, $C_{23}H_{38}O_2(OH)_2$.

The above-mentioned dark brown precipitate amounted to 50 grams, and consisted for the most part of a barium salt. It was treated with acetic acid, when a portion remained undissolved, and this, after being dried, was extracted in a Soxhlet apparatus with absolute alcohol. A small amount of a sparingly soluble substance was thus removed, which, after several crystallisations from dilute pyridine, was obtained in colourless, microscopic needles, melting at 285—290°. After drying at 110°, it was analysed. (Found, C=72·4; H=10·6. Calc., C=72·6; H=10·5 per cent.)

This substance was evidently ipuranol, the identity of which was further confirmed by the colour reactions and the formation of the acetyl derivative, which separated from ethyl acetate in needles melting at 162°.

The liquid from which the above-mentioned dark brown precipitate had been separated by filtration was diluted with a large volume of water, and distilled in a current of steam in order to remove the alcohol. The excess of barium was then removed by carbon dioxide, and, after boiling and filtering, dilute sulphuric acid was added to the liquid until a precipitate just ceased to be produced, any excess of the mineral acid being carefully avoided. The liquid was again filtered to remove the barium sulphate, and then distilled in a current of steam until volatile acids ceased to pass over.

Isolation of d-*α-Methylbutyric and Tiglic Acids.*

The above-mentioned distillate was a slightly opalescent liquid, amounting to about 8 litres. It was neutralised with sodium carbonate, and concentrated to a small volume, then acidified and extracted with ether, the ethereal liquid being dried and the solvent removed. A quantity (40 grams) of liquid acid was thus obtained, which, when distilled under the ordinary pressure, passed over between 160° and 200°, and it was observed that the last portions of the distillate, on cooling, solidified to a colourless, crystalline mass. Although the greater part of the solid acid, which was unsaturated, could be removed from the liquid portion by repeated fractional distillation, a complete separation could not thus be effected. In order, therefore, to obtain the liquid acid in a pure state, it was finally treated with potassium permanganate in alkaline solution at 0°. On subsequently recovering the unchanged acid, it was found to distil at 172—175°, and to possess the odour of a valeric acid. (Found, $C=58{\cdot}6$; $H=10{\cdot}0$. Calc., $C=58{\cdot}8$; $H=9{\cdot}8$ per cent.)

The density of the acid was 0·9392 at 21°, and a determination of its specific rotatory power gave the following result:

α_D, in a 25 mm. tube at 21°, $= +4°8'$, whence $[\alpha]_D + 17{\cdot}6°$.

It was thus evident that the above-described liquid consisted of the optically active valeric acid (*d*-*α*-methylbutyric acid), which had previously been obtained from several convolvulaceous resins.

The solid acid which separated from the final fractions of the above-mentioned volatile acids was collected, and recrystallised from water, when it separated in flat needles, melting at 64—65°. By the slow evaporation of its ethereal solution it was obtained in large, well-defined prisms. It instantly decolorised an alkaline solution of potassium permanganate at 0°, and was therefore unsaturated. (Found, $C=59{\cdot}9$; $H=8{\cdot}2$. Calc., $C=60{\cdot}0$; $H=8{\cdot}0$ per cent.)

This substance was thus identified as tiglic acid.

The aqueous liquid, from which the above-described acids had been extracted with ether, was distilled in a current of steam. The distillate contained formic acid, together with apparently a little valeric acid.

Non-volatile Products of the Alkaline Hydrolysis.—After the removal of the *d*-*α*-methylbutyric and tiglic acids by distillation with steam, as above described, there remained in the distillation flask a dark yellow liquid, which was filtered and concentrated under diminished pressure to the consistency of a viscid syrup.

This product amounted to 327 grams. When further dried it could be reduced to a light brown powder, which, however, became viscid on exposure to the air. It was freely soluble in water, and did not reduce Fehling's solution until after boiling with a dilute mineral acid.

The total amount of the above-mentioned syrupy product was dissolved in alcohol, mixed with purified sawdust, and the thoroughly dried mixture extracted successively in a Soxhlet apparatus with light petroleum, ether, chloroform, ethyl acetate, and alcohol. The light petroleum removed nothing, and, after extracting with the three succeeding solvents, nothing further was removed by the alcohol.

Ether and Chloroform Extracts of the Hydrolysed Resin (II).

These extracts were dark-coloured, viscid masses, amounting to 25 and 2 grams respectively. They were sparingly soluble in water, and after heating with a 5 per cent. solution of sulphuric acid in aqueous alcohol, nothing definite could be isolated. The liquids obtained by this treatment reduced Fehling's solution, but no osazone could be prepared from them.

Ethyl Acetate Extract of the Hydrolysed Resin (II).

This was a colourless, semi-crystalline mass, amounting to 300 grams. When thoroughly dried, it could be reduced to a fine, white powder, which was not hygroscopic. It was only sparingly soluble in ethyl acetate, even when hot, but readily soluble in alcohol, acetone, and water. The aqueous solution was optically active, and a determination of its specific rotatory power gave the following result:

0·7750, made up to 20 c.c. with distilled water, gave α_D $-2°55'$ in a 2-dcm. tube, whence $[\alpha]_D$ $-37·62°$.

A quantity (200 grams) of the above-described product was heated for about three hours in a reflux apparatus with ten times its weight of aqueous 5 per cent. sulphuric acid, and the liquid then distilled in a current of steam. The distillate, which amounted to 3 litres, was first extracted with ether, when a small amount of an oil was removed, which partly solidified. The oily portion gave the colour reaction for furfuraldehyde, whilst the solid substance, which separated from ethyl acetate in laminæ melting at 44°, appeared to consist of methyl jalapinolate, a compound which was obtained in somewhat larger amount from the non-volatile products of the acid hydrolysis. The aqueous distillate, after extraction with ether, was found to contain a little formic acid, with apparently traces of a valeric acid.

After the removal of the volatile products resulting from the above-described acid hydrolysis, there remained in the distillation flask about 3 litres of a dark yellow liquid, together with a quantity of solid material which floated on the surface. The whole was extracted with ether, when all of the solid material passed into solution. On subsequently extracting the ethereal liquid with aqueous sodium carbonate, a quantity of the sodium salt of an organic acid separated, and this was collected. The ethereal liquid was then dried, and the solvent removed, when a small amount (0·5 gram) of a light-coloured oil remained, which became solid on cooling. This substance was recrystallised from ethyl acetate, when it separated in shining laminæ, melting at 45—46°:

0·1250 gave 0·3244 CO_2 and 0·1350 H_2O. C=70·8; H=12·0.

$C_{17}H_{34}O_3$ requires C=71·3; H=11·9 per cent.

On heating a portion of the substance with alcoholic potassium hydroxide it was found to become hydrolysed, and an acid was thus obtained, which separated from ethyl acetate in small needles, melting at 67—68°. (Found, C=70·2; H=11·8. Calc., C=70·6; H=11·7 per cent.)

The above-described substance was thus identified as methyl jalapinolate, which had evidently escaped hydrolysis by the preceding treatment with dilute sulphuric acid.

Small amounts of methyl jalapinolate were subsequently isolated from the various products resulting from the alkaline hydrolysis of the original ethyl acetate extract of the resin. It was therefore deemed of interest to ascertain what proportion of the hydrolysed ethereal extract of the original resin was acidic, as a portion of it evidently consisted of a derivative of methyl jalapinolate. For this purpose a quantity (10 grams) of the hydrolysed resin was acetylated by means of acetic anhydride, the product dissolved in ether, and the ethereal liquid shaken with aqueous potassium hydroxide. By this means 6·7 grams of acidic material were removed, which formed a yellow, amorphous, friable mass, and on subsequently evaporating the ether, 6·4 grams of a neutral, light yellow syrup were obtained. After hydrolysis with barium hydroxide the product from the acidic portion had $[\alpha]_D$ −35·7°, whilst that from the neutral portion had $[\alpha]_D$ −35·1°. Both these products, on heating with dilute sulphuric acid, yielded jalapinolic acid and a mixture of sugars, the neutral acetyl derivative also giving a trace of methyl jalapinolate.

Isolation of Jalapinolic Acid, $C_{15}H_{30}(OH)\cdot CO_2H$.
(*Hydroxyhexadecylic Acid.*)

The sodium salt, obtained by extracting the ethereal liquid with sodium carbonate, as above described, was decomposed with dilute sulphuric acid, and the liberated organic acid taken up with ether. On removing the solvent, a quantity (62 grams) of an oily product was obtained, which solidified on cooling to a crystalline mass. This was dissolved in alcohol, mixed with purified sawdust, and the thoroughly dried mixture extracted successively with (*a*) light petroleum, and (*b*) ether.

(*a*) *Petroleum Extract.*—This was a white, fatty mass, amounting to 48 grams. It was converted into the methyl ester by dissolving in methyl alcohol and saturating the solution with dry hydrogen chloride. On subsequently pouring the acid liquid into water, and extracting with ether, a product was obtained, which, when distilled under diminished pressure, passed over at 220°/20 mm. as a colourless oil, and, on cooling, solidified to a white, crystalline mass. On recrystallising the distilled ester from ethyl acetate, it separated in handsome laminæ, melting at 47—49°. (Found, $C=71{\cdot}0$; $H=11{\cdot}9$. Calc., $C=71{\cdot}3$; $H=11{\cdot}9$ per cent.)

The optical rotatory power of the ester was determined, with the following result:

2·8756, made up to 20 c.c. with chloroform, gave $\alpha_D\ +0°17'$ in a 2-dcm. tube, whence $[\alpha]_D\ +0{\cdot}98°$.

The ester was then hydrolysed by boiling with an alcoholic solution of potassium hydroxide, the alcohol removed, and the liquid acidified, when an acid was obtained, which separated from dilute acetic acid in fine, silky needles, melting at 67—68°. (Found, $C=70{\cdot}7$; $H=11{\cdot}8$. Neutralisation value $=209{\cdot}3$. Calc., $C=70{\cdot}6$; $H=11{\cdot}7$ per cent. Neutralisation value $=206{\cdot}2$.)

The above-described acid is thus seen to be jalapinolic acid, a compound which was first obtained by Mayer from "jalapin" (*Annalen*, 1855, **95**, 149), and subsequently investigated by Kromer (*J. pr. Chem.*, 1898, [ii], **57**, 448). The last-mentioned investigator stated that jalapinolic acid is optically inactive, which is not correct, although its rotatory power is comparatively small *:

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* Having observed the optical activity of jalapinolic acid, it seemed desirable to examine in this respect two other hydroxy-acids which had previously been obtained from convolvulaceous resins, namely: convolvulinolic acid (*J. Amer. Chem. Soc.*, 1910, 32, 106) and ipurolic acid, (*ibid.*, p. 107, and *Amer. J. Pharm.*, 1908, **80**, 273).

Convolvulinolic acid, $C_{14}H_{28}(OH)\cdot CO_2H$ (m. p. 51—52°): 4·1738, made up to 20 c.c. with chloroform, gave $\alpha_D+0°35'$ in a 2-dcm. tube, whence $[\alpha]_D+1{\cdot}39°$.

3·5518, made up to 20 c.c. with chloroform, gave $\alpha_{\mathrm{D}} + 0^\circ 17'$ in a 2-dcm. tube, whence $[\alpha]_{\mathrm{D}} + 0 \cdot 79^\circ$.

(*b*) *Ethereal Extract.*—The acid extracted by ether was dark in colour, and amounted to 12 grams. It was purified by conversion into its methyl ester, and found to consist only of jalapinolic acid.

Identification of Dextrose and a Methylpentose.

The aqueous acid liquid resulting from the acid hydrolysis of the ethyl acetate extract of the hydrolysed resin, which had been extracted with ether as above described, was subsequently treated with barium hydroxide for the removal of the sulphuric acid, the mixture filtered, and the filtrate evaporated under diminished pressure to the consistency of a syrup. This syrup readily reduced Fehling's solution, and yielded an osazone, melting at 203—205°, which was evidently *d*-phenylglucosazone.

In order to obtain more definite information respecting the character of the sugar produced by the above-mentioned hydrolysis, the syrup was heated with acetic anhydride in the presence of a trace of *d*-camphorsulphonic acid. A vigorous reaction ensued, and after this had subsided the mixture was cooled, poured into water, and the liquid extracted with ether. The ethereal liquid was washed, dried, and the solvent removed, when a quantity of a light-coloured syrup remained, which was dissolved in dilute alcohol. After keeping for a few days a crystalline substance separated, which was collected and recrystallised from 70 per cent. alcohol, when it was deposited in handsome, prismatic needles, melting at 142—143°. It was anhydrous, and gave on analysis the following results:

0·2466 gave 0·4582 CO_2 and 0·1358 H_2O. C = 50·6; H = 6·1.
0·1070 „ 0·1986 CO_2 „ 0·0606 H_2O. C = 50·6; H = 6·3.
$C_{14}H_{20}O_9$ requires C = 50·6; H = 6·0 per cent.

The above-described substance is thus seen to be a *tetra-acetylmethylpentose*, $C_6H_8O_5(CO{\cdot}CH_3)_4$, and it is apparently a new compound. A determination of its optical rotatory power gave the following result:

Methyl convolvulinolate, $C_{14}H_{28}(OH){\cdot}CO_2{\cdot}CH_3$ (m. p. 32—33°): 2·0142, made up to 20 c.c. with chloroform, gave $\alpha_{\mathrm{D}} + 0^\circ 19'$ in a 2-dcm. tube, whence $[\alpha]_{\mathrm{D}} + 1 \cdot 57^\circ$.

Ipurolic acid, $C_{13}H_{25}(OH)_2{\cdot}CO_2H$ (m. p. 100—101°).

No rotation could be measured with a solution of 2·6068 of the acid in 20 c.c. of absolute alcohol.

Methyl ipurolate, $C_{13}H_{25}(OH)_2{\cdot}CO_2{\cdot}CH_3$ (m.p. 68—69°): 0·6900, made up to 20 c.c. with absolute alcohol, gave $\alpha_{\mathrm{D}} + 0^\circ 7'$ in a 2-dcm. tube, whence $[\alpha]_{\mathrm{D}} + 1 \cdot 69^\circ$.

0·7238, made up to 20 c.c. with chloroform, gave α_D +1°34′ in a 2-dcm. tube, whence $[\alpha]_D$ +21·64°.

The sugar obtained by hydrolysing a small portion of the above-described acetyl derivative yielded an osazone melting at 180—182°, but this was not identical with rhamnosazone, for a mixture of the two compounds melted at 163—164°. Moreover, on acetylating a quantity of pure rhamnose no crystalline derivative could be obtained.

For the purpose of comparing the properties of the sugar yielding the above-described tetra-acetyl derivative with those of rhodeose, a small quantity of the latter was kindly supplied to us by Professor E. Votoček, of Prague. This substance was in colourless, prismatic needles, melting at 144—145°, but the acetylated product could only be obtained in the form of a syrup. It may, furthermore, be noted that the phenylosazone of rhodeose has been recorded as melting at 170° (*Chem. Centr.*, 1900, I., p. 803). *iso*Rhodeose yields an osazone melting at 186—187°, but the benzoylated product could not be obtained in a crystalline state (Votoček, *Ber.*, 1911, **44**, 820). In order to ascertain whether the methylpentose contained in the above-mentioned syrup was capable of yielding a crystalline benzoyl derivative, portions of the syrup were treated by both the Schotten-Baumann method and by heating with benzoic anhydride, but in each case with a negative result.

After the separation of the above-described tetra-acetylmethylpentose, the mother liquors yielded a further quantity of the same substance, and finally a more readily soluble solid was deposited. This was collected, washed with a little dilute alcohol, and then recrystallised from 70 per cent. alcohol, when it separated in slender needles, melting at 111—112°. After two further crystallisations the substance began to melt at 112°, but complete fusion only took place at 118°. (Found, C=49·2; H=5·7. Calc., C=49·2; H=5·6 per cent.)

This compound was thus identified as penta-acetyldextrose, $C_6H_7O_6(CO{\cdot}CH_3)_5$, and it apparently consisted of a mixture of the α- and β-forms, which melt at 112° and 134° respectively.

From the above results it is evident that by the acid hydrolysis of the ethyl acetate-soluble portion of the hydrolysed ethereal extract of the resin, two sugars are produced, one of which is dextrose, and in predominating amount, whilst the other is a methylpentose.

Oxidation of the Ethyl Acetate Extract of the Hydrolysed Resin with Nitric Acid.

A quantity (25 grams) of the previously-described ethyl acetate extract of the hydrolysed resin was dissolved in a little water, and to the solution, contained in a flask provided with a reflux condenser, 200 grams of nitric acid (D 1·4) were added. The mixture was then gently warmed, when a vigorous reaction ensued, and after this had ceased the heating was continued for a short time. About 200 c.c. of water were subsequently added, the mixture boiled for ten minutes, and then distilled in a current of steam. The distillate was rendered alkaline with sodium carbonate, concentrated to a small bulk, then acidified with hydrochloric acid, and extracted with ether, the ethereal liquid being washed, dried, and the solvent removed. A small amount (1·2 grams) of a liquid acid was thus obtained, which, when distilled under the ordinary pressure, passed over between 190° and 195° as a colourless oil, and was dextrorotatory:

0·1578 gave 0·3494 CO_2 and 0·1434 H_2O. C = 60·3; H = 10·1.
$C_5H_{10}O_2$ requires C = 58·8; H = 9·8 per cent.
$C_6H_{12}O_2$ „ C = 62·0; H = 10·3 „ „

A portion of the acid was converted into a silver salt, which was precipitated in three fractions, and these were analysed:

(*a*) 0·3020 gave 0·1456 Ag. Ag = 48·2.
(*b*) 0·2962 „ 0·1440 Ag. Ag = 48·6.
(*c*) 0·2320 „ 0·1180 Ag. Ag = 50·9.
$C_5H_9O_2Ag$ requires Ag = 51·7 per cent.
$C_6H_{11}O_2Ag$ „ Ag = 48·4 „ „

It would thus appear that the volatile acid formed by the oxidation consisted of a mixture of optically active valeric acid and a hexoic acid.

The aqueous acid liquid remaining in the distillation flask deposited a white solid on cooling. The mixture was accordingly extracted with ether, and the ethereal liquid shaken with aqueous sodium carbonate, which removed all of the dissolved substance. On subsequently acidifying the alkaline liquid and extracting with ether, it yielded a quantity (3 grams) of a solid acid, which was fractionally crystallised, first from dilute acetic acid, and finally from the glacial acid. Four fractions were thus obtained, which melted at 125—127°, 115—117°, 104—107°, and 84—90° respectively. After drying in a vacuum and then at 120°, they were analysed:

I. 0·0956 gave 0·2092 CO_2 and 0·0792 H_2O. C=59·6; H=9·2.
II. 0·1084 „ 0·2358 CO_2 „ 0·0884 H_2O. C=59·3; H=9·0.
III. 0·1434 „ 0 3176 CO_2 „ 0·1190 H_2O. C=60·4; H=9·2.
IV. 0·1704 „ 0·3730 CO_2 „ 0·1394 H_2O. C=59·7; H=9·1.
$C_{10}H_{18}O_4$ requires C=59·4; H=8·9 per cent.
$C_{11}H_{20}O_4$ „ C=61·1; H=9·3 „ „

These results would thus indicate that the non-volatile acids produced by the oxidation of the above-described glucosidic substance consist of a mixture of sebacic and *n*-nonanedicarboxylic acids. The first mother liquors from the crystallisation of these acids also contained a small amount of oxalic acid, which was evidently produced from the sugar complex of the glucoside.

Kromer (*J. pr. Chem.*, 1898, [ii], **57**, 448), in investigating the jalapinolic acid obtained from the so-called "false jalap," observed it to yield, on oxidation with alkaline potassium permanganate, α-methylbutyric and sebacic acids, together with an acid melting at 89—91°, which was thought to be isomeric with the latter. From these results he concluded that the constitution of jalapinolic acid could be represented as follows: $CHMeEt{\cdot}CH(OH){\cdot}[CH_2]_{10}{\cdot}CO_2H$.

As already noted, it has now been ascertained that jalapinolic acid is optically active, but inasmuch as the oxidation products of the above-described glucosidic substance appear to consist most largely of sebacic acid and a hexoic acid, it is more probable that the respective acid possesses the following formula:

$$CHMeEt{\cdot}CH_2{\cdot}CH(OH){\cdot}[CH_2]_9{\cdot}CO_2H.$$

III.—*Chloroform Extract of the Resin.*

This was a dark, resinous product, amounting to only 8 grams. It was heated with dilute sulphuric acid in aqueous alcohol, but no crystalline substance could be isolated after this treatment, and although the resulting aqueous liquid reduced Fehling's solution, no osazone could be prepared from it.

IV.—*Ethyl Acetate Extract of the Resin.*

This extract, after the removal of the solvent, formed a dark-coloured mass, and amounted to 295 grams. When dissolved in alcohol, and treated with animal charcoal, a product was obtained which could be reduced to a nearly white powder. Its optical rotatory power was determined, with the following result:

A solution in absolute alcohol, of which 5 c.c. contained 0·5086 gram of substance, gave α_D −2°51′ in a 1-dcm. tube, whence $[\alpha]_D$ −28·01°.

Hydrolysis of the Ethyl Acetate Extract with Barium Hydroxide.

A quantity (250 grams) of the ethyl acetate extract of the resin was dissolved in alcohol, a little water added, and subsequently a slight excess of a cold saturated solution of barium hydroxide. The hydrolysis was then allowed to proceed in precisely the same manner as described in connexion with the ether extract of the resin. After the hydrolysis was complete the filtered liquid was diluted with a large volume of water, and the alcohol removed by distillation in a current of steam. The barium contained in the solution was then exactly precipitated with dilute sulphuric acid, and the filtered liquid again distilled in steam until acid ceased to pass over. The distillate was rendered alkaline with sodium carbonate, concentrated to a small volume, then acidified, and extracted with ether. The aqueous liquid remaining after this treatment was found to contain a considerable amount of acetic acid, but no formic acid. On subsequently evaporating the ethereal liquid, a quantity (15 grams) of a colourless liquid acid was obtained, which was distilled under the ordinary pressure, and the following fractions collected: (1) 100—125°; (2) 125—150°; (3) 150—170°; (4) 170—180°; (5) 180—185°; (6) 185—195°. The last fraction, amounting to 0·5 gram, almost completely solidified.

It was evident from the above results that the volatile acids consisted of a rather complex mixture. Fractions 1, 2, and 3 were each converted into three fractions of silver salt, the analysis of which indicated the presence of a considerable proportion of acetic acid with apparently some valeric acid. Fractions 4, 5, and the liquid portion of 6 were united, and treated in alkaline solution with potassium permanganate, as described in connexion with the volatile acids obtained by the hydrolysis of the ethereal extract of the resin with barium hydroxide. The amount of acid recovered after this treatment was 4·1 grams. It distilled between 173° and 175°, and possessed the following constants: D^{21} 0·9320; α_D $+4°7'$ in a 25 mm. tube, whence $[\alpha]_D$ $+17·6°$. (Found, C = 57·6; H = 9·7. Calc., C = 58·8; H = 9·8 per cent.)

The above-described acid thus appears to have consisted chiefly of the optically active valeric acid, with a little acetic acid.

The solid acid contained in fraction 6 was recrystallised from water, when it separated in needles melting at 64—65°, and was identified as tiglic acid. (Found, C = 60·0; H = 8·2. Calc., C = 60·0; H = 8·0 per cent.)

The aqueous liquid remaining in the distillation flask after the removal of the above-mentioned volatile acids was filtered, and concentrated under diminished pressure to a syrup. The latter was then dissolved in alcohol, mixed with purified sawdust, and the thoroughly dried mixture successively extracted in a Soxhlet apparatus with ether, chloroform, ethyl acetate, and alcohol.

Ether and Chloroform Extracts of the Hydrolysed Resin (IV).

These extracts were dark-coloured syrups, amounting to 12·5 and 2·3 grams respectively. They were only sparingly soluble in water, and were therefore heated with 5 per cent. sulphuric acid in aqueous alcohol. In both cases a very small amount of methyl jalapinolate was isolated from the neutral non-volatile portion of the product, and from the ethereal extract a small amount of jalapinolic acid was also obtained.

Ethyl Acetate Extract of the Hydrolysed Resin (IV).

This was an amorphous solid, which could easily be reduced to a light-coloured powder, and was not hygroscopic. It was readily soluble in cold water, yielding a clear liquid, which did not reduce Fehling's solution until after heating with an acid. It was optically active, and a determination of its specific rotatory power gave the following result:

> A solution, of which 5 c.c. gave on evaporation 0·1650 gram of substance, dried at 110°, had α_D $-2°9'$ in a 2-dcm. tube, whence $[\alpha]_D$ $-32·62°$.

Treatment with Dilute Sulphuric Acid.—A solution containing 25 grams of the above-described product in 500 grams of 5 per cent. aqueous sulphuric acid, was heated for about four hours in a reflux apparatus, and the liquid then distilled in a current of steam. The volatile product appeared to consist only of traces of furfuraldehyde and formic acid.

After the above operation there remained in the distillation flask a dark yellow liquid with a cake of solid substance floating on the surface. The whole was extracted with ether, and the ethereal liquid shaken with a solution of sodium carbonate. On subsequently evaporating the ether, a small amount of a neutral substance was obtained, which, when recrystallised from ethyl acetate, separated in leaflets melting at 45—46°, and was identified as methyl jalapinolate. The sodium carbonate extract was then acidified and extracted with ether, when a quantity of a dark-coloured product was obtained. This was dissolved in alcohol, mixed with purified sawdust, and the dried mixture extracted successively with light petroleum and ether. The petroleum removed a quantity (3 grams) of a white solid, which, when crystallised from dilute acetic acid, separated in needles melting at 67—68°, and proved to be jalapinolic acid, $C_{16}H_{32}O_3$. (Found, C = 70·5; H = 11·8. Calc., C = 70·6; H = 11·7 per cent.) A large amount of this acid had previously been obtained from the ethereal extract of the original resin after alkaline hydrolysis and extraction with ethyl acetate.

By the subsequent extraction of the above-mentioned mixture with ether, a further quantity (about 2 grams) of an acidic product was obtained, which was dark in colour. It was therefore purified by conversion into its methyl ester, which distilled at 220/20 mm., and, after crystallisation from ethyl acetate, melted at 47—49°. The portion of acidic product removed by ether was thus shown to consist of impure jalapinolic acid.

The above-described yellow aqueous liquid, which had been extracted with ether, was finally treated with barium hydroxide for the removal of the sulphuric acid, and, after filtration, was concentrated under diminished pressure. It then yielded an osazone, which separated from dilute pyridine in clusters of fine needles, melting at 180—182°, and was doubtless a derivative of the previously described methylpentose. No dextrose was present in the liquid.

Alcohol Extract of the Hydrolysed Resin (IV).

This was an amorphous solid, which amounted to 100 grams, and, after treatment with animal charcoal, was obtained as a perfectly white powder. It was readily soluble in water, and did not reduce Fehling's solution until after heating with an acid. It was optically active, and a determination of its specific rotatory power gave the following result:

A solution, of which 5 c.c. gave on evaporation 0·3200 gram of substance, dried at 110°, had α_D −4°26′ in a 2-dcm. tube, whence $[\alpha]_D$ −34·64°.

Treatment with Dilute Sulphuric Acid.—Seventy grams of the above-described product were dissolved in water, and such an amount of dilute sulphuric acid added as to form 1200 grams of solution containing 5 per cent. of acid. The whole was then heated in a reflux apparatus for about four hours, after which it was distilled in a current of steam. The only volatile products obtained by this treatment were a little oil giving the colour reaction of furfuraldehyde and a small amount of formic acid.

After the above operation there remained in the distillation flask a dark yellow liquid and a quantity of solid substance floating on the surface. The whole was extracted with ether, and the ethereal liquid shaken with aqueous sodium carbonate. On evaporating the ether, a small amount of substance was obtained, which, when crystallised from ethyl acetate, separated in leaflets melting at

45—46°, and was evidently methyl jalapinolate. The sodium carbonate extract, when acidified and extracted with ether, yielded a quantity of acid, which was dissolved in alcohol, mixed with purified sawdust, and extracted successively with light petroleum and ether, as described in connexion with the corresponding product from the ethyl acetate extract of the hydrolysed resin (IV). The petroleum extract amounted to 2·5 grams, and after crystallisation from dilute acetic acid was obtained in colourless needles, melting at 67—68°. This substance consisted of pure jalapinolic acid, $C_{16}H_{32}O_3$. (Found, C = 70·6; H = 11·8. Calc., C = 70·6; H = 11·7 per cent.) The acid contained in the ethereal extract, being dark in colour, was converted into its methyl ester, and the product distilled under diminished pressure, when it passed over at 220°/20 mm. as a nearly colourless oil, which solidified on cooling to a crystalline mass. It was recrystallised from ethyl acetate, when it separated in beautiful, colourless laminæ, melting at 47—49°. The amount of this ester was 13 grams, and it consisted of methyl jalapinolate.

The yellow aqueous liquid which had been extracted with ether as above described, was treated with barium hydroxide for the removal of the sulphuric acid, and, after filtration, concentrated under diminished pressure. The resulting syrup when treated by the method described by A. G. Perkin (Trans., 1910, **97**, 1777) yielded two osazones, one of which, and the larger in amount, melted at 203—205°, and was doubtless *d*-phenylglucosazone, whilst the other, after crystallisation from dilute pyridine, melted at 180—182°. The compound melting at 180—182° was not rhamnosazone, but evidently derived from another methylpentose, inasmuch as a portion of the above-mentioned syrup, when treated with acetic anhydride, yielded the same crystalline tetra-acetyl derivative (m. p. 142°) as has already been described in connexion with the portion of the hydrolysed ethereal extract of the resin (II) which was soluble in ethyl acetate. Penta-acetyldextrose (m. p. 112°) was also obtained by this treatment.

V.—*Alcohol Extract of the Resin.*

This was a black, amorphous solid, amounting to 20 grams. When heated with dilute sulphuric acid in aqueous alcohol, it yielded traces of formic acid and a sugar from which *d*-phenylglucosazone (m. p. 204—205°) was prepared. It was therefore glucosidic in character.

Summary.

The material employed for this investigation consisted of the roots of *Ipomoea orizabensis*, Ledanois (Nat. Ord. *Convolvulaceae*), which are commonly known as "Mexican Scammony Root."

The root was found to contain 14·55 per cent. of resin, 71 per cent. of which was soluble in ether. After treatment with animal charcoal the resin was obtained nearly colourless. It then melted at 125—130°, and had $[\alpha]_D - 23·0°$.

For a complete examination of the root, 48·76 kilograms of the ground material were extracted with hot alcohol. A portion of the concentrated extract was employed for determining the presence of sucrose, and a small amount of the latter was isolated. Another portion of the extract was distilled in a current of steam, when a very small amount of a pale yellow essential oil was obtained. From the portion of the extract which was soluble in water, the following compounds were isolated: (i) scopoletin, $C_{10}H_8O_4$ (m. p. 203—204°), a small proportion of which appeared to be present in the form of a glucoside; (ii) 3:4-dihydroxycinnamic acid, $C_9H_8O_4$ (m. p. 223—225°), from which the *methyl*-ester (m. p. 158—160°) was prepared. The aqueous liquid contained, furthermore, a quantity of sugar, which yielded *d*-phenylglucosazone (m. p. 205—206°).

The portion of the alcoholic extract which was insoluble in water consisted of a resin which possessed the above-mentioned characters. The resin was first successively extracted with various solvents, and the resulting extracts were then further examined.

I. *Petroleum Extract of the Resin.*—From this extract the following substances were obtained: (i) hentriacontane, $C_{31}H_{64}$; (ii) a phytosterol, $C_{27}H_{46}O$; (iii) cetyl alcohol, $C_{16}H_{34}O$; (iv) a mixture of fatty acids, consisting of palmitic, stearic, oleic, and linolenic acids.

II. *Ethereal Extract of the Resin.*—The optical rotatory power of this extract was $[\alpha]_D - 20·5°$. After hydrolysis with barium hydroxide it yielded: (i) ipuranol, $C_{23}H_{38}O_2(OH)_2$; (ii) *d*-α-methylbutyric acid; (iii) tiglic acid; and a product which on acid hydrolysis gave (iv) jalapinolic acid, $C_{15}H_{30}(OH)·CO_2H$ (m. p. 67—68°; $[\alpha]_D + 0·79°$), together with a little methyl jalapinolate, and (v) a mixture of sugars, consisting of dextrose and a methylpentose. The latter yielded an osazone melting at 180—182°, and a *tetra-acetyl* derivative, $C_6H_8O_5(CO·CH_3)_4$, which apparently is a new compound. This derivative crystallises in handsome, prismatic needles, melting at 142—143°, and has $[\alpha]_D + 21·64°$. The ethyl acetate extract of the product resulting from the alkaline hydrolysis of the ethereal extract of the resin gave on oxidation with nitric acid a mixture of acids, consisting apparently of optically active valeric and hexoic acids, together with sebacic and *n*-nonanedicarboxylic acids.

III. *Chloroform Extract of the Resin.*—This was relatively small in amount, and consisted of a dark resinous product.

IV. *Ethyl Acetate Extract of the Resin.*—The optical rotatory power of this extract was $[\alpha]_D -28{\cdot}01°$. After hydrolysis with barium hydroxide it yielded products from which the same substances were obtained as from the ethereal extract of the resin, with the exception of the small amount of ipuranol.

V. *Alcohol Extract of the Resin.*—This was a black, amorphous product of a glucosidic nature, but which yielded nothing definite on hydrolysis.

From the results of the present investigation it will be apparent that the resin of *Ipomoea orizabensis* is an exceedingly complex mixture, the constituents of which are, for the most part, amorphous, and not entirely glucosidic. It follows, therefore, that the so-called "jalapin," which includes all the constituents of the resin that are soluble in ether, cannot be represented by any of the various formulæ hitherto assigned to it. It may also be noted that the portion of this resin which is soluble in ether is not identical with the ether-soluble portion of jalap resin, as has previously been affirmed.

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II.—*The Influence of Neutral Solvents on Velocity of Reaction. Part I. Transformation of Anis*-syn*aldoxime in Various Solvents.*

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A FEW years ago, Patterson and McMillan (Trans., 1907, **91**, 504; 1908, **93**, 1041; *Ber.*, **40**, 2564; *Proc. Roy. Phil. Soc. Glasgow*, 1910–11, **42**, 26) devised a method for following quantitatively, by means of the polarimeter, certain desmotropic changes. The method consisted in dissolving a labile substance in an optically active solvent, and observing the gradual change in rotation of the solution as the alteration in constitution of the inactive solute proceeded. In this way the velocity of transformation of *syn*- into *anti*-oximes

(Trans., 1907, **91**, 504; *Ber.*, 1907, **40**, 2564); of ω-*iso*nitrotoluene into ω-nitrotoluene (Trans., 1908, **93**, 1048); of the α- or enol- into the β- or aldo-form of phenylformylacetic ester (Trans., 1907, **91**, 519), and of other changes, has been measured.

In the first of these papers it was also shown that the method was one by means of which the effect of indifferent solvents on the velocity of these apparently unimolecular reactions could be examined. To similar solutions of anis*syn*aldoxime in ethyl tartrate there were added respectively, equal volumes of *iso*butyl alcohol, of chloroform, and of benzene, when it was found that not only was the total change of rotation which occurred in each case quite different, but that the velocity of reaction was different also. In view of the interest which attaches to the influence of solvents in modifying the velocity of chemical reactions, we thought it desirable to extend this part of the investigation. In the present paper we give a description of our method and results, and conclude with a short comparison of the latter with the results of other investigators in this field.

The ethyl tartrate was prepared by the hydrogen chloride saturation method. The anis*syn*aldoxime was prepared in the usual way on the afternoon previous to its use. On the morning of the experiment it was recrystallised from benzene, and quickly dried on porous plate in an evacuated desiccator over sulphuric acid. The experiments were done in duplicate, always with separately recrystallised, and often with freshly prepared, *syn*oxime. The melting point of the sample used lay, almost invariably, between 135° and 137°.

In order to determine the most favourable conditions for convenient work, we made a few preliminary experiments, and determined, in the first place, the rate of transformation of the pure anis*syn*aldoxime in the ethyl tartrate alone, with the results quoted in table I on p. 28.

A solution was then made up of 5 c.c. of ethyl tartrate and 5 c.c. of methyl alcohol with 5 per cent. by weight of anis*syn*aldoxime, but the total change of rotation in a day, at 20°, was only 0·3°, and after several days it was only 0·4°. This is too small a change to work upon, so a similar solution, but containing 10 per cent. of oxime, was tried. This, however, only gave a total change of 0·67°, still undesirably small. We therefore reduced the proportion of indifferent solvent in the mixture, and made up a solution of 75 per cent. by volume of ethyl tartrate and only 25 per cent. by volume of methyl alcohol, to which was added 5 per cent. of anis*syn*aldoxime. The change observed in the first day in this case was 0·7°, whilst the total change was over 1°; but the time which elapsed

TABLE I.

*Anissynaldoxime in Ethyl Tartrate.**

I: $p=96{\cdot}13$; $a=2{\cdot}61°$.

T (min.).	α_D^{20}.	1000 k.
0	+13·32°	—
67	13·212	0·64
133	13·126	0·58
164	13·056	0·65
219	12·99	0·62
234	12·975	0·61
271	12·925	0·61
309	12·87	0·61
∞	10·71	—
	Mean......	0·62

II: $p=96{\cdot}17$; $a=2{\cdot}61°$.

T (min.).	α_D^{20}.	1000 k.
0	+13·32°	—
31	13·268	0·671
49	13·236	0·66
61	13·222	0·63
75	13·202	0·61
88	13·174	0·65
107	13·136	0·69
185	13·036	0·62
212	13·010	0·59
231	12·977	0·61
261	12·940	0·60
290	12·90	0·61
313	12·87	0·60
360	12·81	0·60
∞	10·71	—
	Mean......	0·63

* In this and the following tables, p indicates grams of ethyl tartrate per 100 grams of solution; a is the total change of rotation from time 0 to time ∞. The initial rotation is got by extrapolation from the other data.

before the transformation could be considered at an end was so great that we decided to work at a higher temperature, more especially as the room temperature was apt, occasionally, to rise a little above 20°. Therefore, starting afresh, the velocity constant was determined in undiluted ethyl tartrate at 26°, with the following results:

TABLE II.

Anissynaldoxime in Ethyl Tartrate.

No. of solution.	p.	d.	1000 k.	1000 k. [Mean of two series.]
III.	96·17	2·32°	1·71	—
IV.	96·17	2·30	1·78	*1·745*

The total change of rotation at 26° (2·31°) is thus less than at 20° (2·61°), but the transformation is about three times as rapid. The ethyl tartrate used had α_D^{26} +10·074°. The temperature was kept constant within 0·05°. The solvents were all carefully distilled over sodium,* and the solutions were made up as follows: 15 c.c. ethyl tartrate were delivered from a pipette into a small flask and weighed. To this were added 5 c.c. of the solvent, and the flask and contents again weighed. This mixture of ethyl tartrate and solvent was divided into two approximately equal parts, each being weighed; these were used on successive days. To each part, as nearly as possible 4·76 per cent., *by weight*, of *syn*aldoxime was added.* Immediately the oxime had dissolved the solution was transferred to a 100 mm. polarimeter tube, which had been lying for some time previously in the thermostat of the polarimeter to acquire the desired temperature, the first reading being usually made after the lapse of about an hour. The results obtained with methyl alcohol, ethyl alcohol, *n*-propyl alcohol, *iso*butyl alcohol, allyl alcohol, benzyl alcohol, and water are recorded in the following tables, the data for the first-named being given in full, whilst the remainder are summarised:

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* Except allyl alcohol and benzyl alcohol, which were digested with fused potassium carbonate and distilled.

TABLE III.

*Transformation of Anis*syn*aldoxime in Presence of Ethyl Tartrate and Methyl Alcohol.*

V: E.T.:S.:O.=
77·86:17·38:4·76; $a=1·174°$.

T (min.)	α_D^{26}.	1000 k.
0	+10·82°	—
78	10·645	2·07
140	10·51	2·19
168	10·478	2·05
192	10·43	2·12
230	10·37	2·12
271	10·32	2·05
300	10·27	2·11
320	10·25	2·08
∞	9·646	—
	Mean......	2·10

VI: E.T.:S.:O.=
77·86:17·37:4·77; $a=1·096°$.

T (min.)	α_D^{26}.	1000 k.
0	+10·72°	—
29	10·654	2·14
65	10·580	2·11
129	10·460	2·10
162	10·418	1·99
184	10·370	2·09
250	10·280	2·06
297	10·220	2·05
315	10·200	2·04
∞	9·624	—
	Mean......	2·07

Mean of two series......... 2·085.

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* That is, 4·76 grams of oxime per 100 grams of the mixture of ethyl tartrate, solvent, and oxime. It might, perhaps, have been better to add a constant weight of oxime for a given volume of solution, but this would make practically no difference in the constants obtained.

TABLE IV.

Transformation of Anissynaldoxime in Presence of Ethyl Tartrate and Various Solvents.

		Composition of solution.					1000 k. [Mean of two series.]
Solvent.	No.	E.T. :	S. :	O.	a.	1000 k.	
Ethyl alcohol	VII.	77·99	17·25	4·76	1·31°	1·92	—
,, ,,	VIII.	77·99	17·25	4·76	1·30	1·86	*1·89*
n-Propyl ,,	IX.	77·66	17·58	4·76	1·46	1·775	—
,, ,,	X.	77·67	17·57	4·76	1·49	1·676	*1·725*
*iso*Butyl ,,	XI.	77·79	17·44	4·77	1·43	1·00	—
,, ,,	XII.	77·79	17·45	4·76	1·43	0·975	*0·987*
Allyl ,,	XIII.	76·90	18·34	4·76	1·33	1·626	—
,, ,,	XIV.	76·90	18·34	4·76	1·40	1·620	*1·623*
Benzyl ,,	XV.	73·72	21·51	4·77	2·12	3·14	—
,, ,,	XVI.	73·76	21·51	4·73	2·09	3·42	*3·28*
Water *	XVII.	74·87	21·29	3·84	0·38	8·60	—
,,	XVIII.	74·86	21·29	3·85	0·36	8·79	*8·69*

* In this case, on account of the solubility relationships, it was necessary to use less oxime.

This series of experiments had practically exhausted our stock of ethyl tartrate, and as it was possible that the active ester had been slowly changing with lapse of time, we thought it advisable again to determine the velocity of transformation of the pure oxime in the ester alone, for comparison with the original values. The results are given below.

TABLE V.

Anissynaldoxime in Ethyl Tartrate.

No. of solution.	p.	a.	1000 k.	1000 k. [Mean of two series.].
XIX.	96·15	2·29°	1·85	—
XX.	96·16	2·28	1·85	*1·85*

It will be observed that the velocity constant has the same value in both of these experiments, but that it is distinctly greater than that obtained at the commencement of our work, having increased from 1·745 to 1·85. This has the effect, of course, of making the more recently determined constants relatively greater than the earlier ones, and we thought it worth while to apply a correction, which will be discussed later on.

For the next series of solvents a fresh sample of ethyl tartrate was prepared, which with pure anis*syn*aldoxime gave the following results:

TABLE VI.

*Anis*syn*aldoxime in Ethyl Tartrate.* (Fresh sample.)

No. of solution.	*p.*	*a.*	1000 *k.*	1000 *k.* [Mean of two series.
XXI.	96·14°	2·40°	0·559	—
XXII.	96·15	2·40	0·567	*0·563*

This sample of tartrate had been subjected to a distillation more than that first used, and the effect of this clearly appears in the lower value of the velocity constant. The ester was, in fact, unnecessarily pure, so that our experiments took too long to run to completion. In the following tables it is practically only readings made on the first day of the experiment that have been used in calculating the values of the constant, and generally the tube had to be set aside in a thermostat at 26° for about a week before the rotation ceased to show any change. As an early experiment had shown that benzene considerably hastens the reaction, we did not anticipate that the slowness of the tartrate would be so troublesome as was actually the case. Using this sample of ester, we examined the influence of benzene, *o*-xylene, *m*-xylene, *p*-xylene, mesitylene, toluene, and nitrobenzene, in the order mentioned, on the velocity of transformation of anis*syn*aldoxime.

TABLE VII.

*Transformation of Anis*syn*aldoxime in Presence of Ethyl Tartrate and Various Solvents.*

		Composition of solution.					
Solvent.	No.	E.T. :	S. :	O.	*a.*	1000 *k.*	1000 *k.* [Mean of of two series.]
Benzene	XXIII.	76·54	18·70	4·76	2·57°	1·00	—
,,	XXIV.	76·54	18·70	4·76	2·30	1·03	*1·015*
o-Xylene	XXV.	76·45	18·79	4·76	2·32	0·73	—
,,	XXVI.	76·44	18·79	4·77	2·455	0·754	*0·742*
m-Xylene	XXVII.	76·79	18·44	4·77	2·68	0·813	—
,,	XXVIII.	76·8	18·44	4·76	2·71	0·803	*0·808*
p-Xylene	XXIX.	76·79	18·45	4·76	2·66	0·872	—
,,	XXX.	76·79	18·44	4·77	2·69	0·85	*0·861*
Mesitylene	XXXI.	76·8	18·49	4·71	2·54	0·772	—
,,	XXXII.	76·75	18·48	4·77	2·65	0·765	*0·768*
Toluene	XXXIII.	76·7	18·48	4·82	2·67	0·861	—
,,	XXXIV.	76·75	18·49	4·76	2·63	0·858	*0·859*
Nitrobenzene	XXXV.	71·38	23·86	4·76	2·87	1·15	—
,,	XXXVI.	71·37	23·86	4·77	2·90	1·06	*1·105*

Finally, we made a control experiment with anis*syn*aldoxime and ethyl tartrate alone, in order to ascertain what alteration, if any, had taken place in the tartrate while this second series of experiments was being carried out, and found, as in the previous case, that the ester was distinctly quicker than before, the constant being 0·67 instead of 0·563.

TABLE VIII.

Anissynaldoxime in Ethyl Tartrate.

No.	*p.*	*a.*	1000 *k.*
XXXVII.	96·17	2·356°	0·67

In table IX we have collected together the data observed. In the second column is shown the total change of rotation for each solution. We have here not taken a mean value, but have given the greater of the two changes. When the total change in one experiment is less than in its fellow, it indicates that a little more transformation has occurred before the observations commenced, but this does not influence the value of the velocity constant. It may be noticed that the total change of rotation in the tartrate alone is not strictly comparable with the changes in the presence of the neutral solvents, since in the former case the oxime is influencing 100 per cent. of active ester, and in the latter only 75 per cent.

TABLE IX.

Rate of Transformation of Anissynaldoxime in Various Solvents at 26°.

Solvent.	Total change in rotation.	1000 *k.*	1000 *k.* Corrected for alteration in ethyl tartrate.	1000 *k.* Corrected for alteration in ethyl tartrate and referred to one standard.
1. No diluent.........	2·32°	1·745	1·745	1·745
2. Water..............	0·38	8·69	8·26	8·26
3. Methyl alcohol...	1·174	2·085	2·07	2·07
4. Ethyl alcohol ...	1·31	1·89	1·862	1·86
5. *n*-Propyl alcohol	1·49	1·725	1·687	1·69
6. *iso*Butyl alcohol	1·43	0·987	0·958	0·96
7. Allyl alcohol......	1·40	1·623	1·565	1·56
8. Benzyl alcohol ...	2·12	3·28	3·14	3·14
9. No diluent	2·29	1·85	—	—
1. No diluent.........	2·40	0·563	0·563	1·745
2. Benzene............	2·57	1·015	1·009	3·13
3. Toluene	2·67	0·859	0·752	2·33
4. *o*-Xylene	2·455	0·742	0·708	2·19
5. *m*-Xylene	2·71	0·808	0·754	2·34
6. *p*-Xylene	2·69	0·861	0·786	2·44
7. Mesitylene	2·65	0·768	0·686	2·13
8. Nitrobenzene ...	2·90	1·105	0·947	2·94
9. No diluent	2·356	0·67	—	—

The total change in the case of water is very small, only 0·38°, and, perhaps in consequence of this, the values of *k*, after about one hundred minutes, were not so constant as for the other solvents. The total change is greater in methyl alcohol than in water, and it rises, through ethyl alcohol, to reach a maximum of 1·49° in *n*-propyl alcohol. In *iso*butyl alcohol and in allyl alcohol it is a little less than in *n*-propyl alcohol. It is to be noticed that in the aromatic compounds the total change is markedly greater than in the aliphatic alcohols, the value rising a little from benzene to toluene and to *m*-xylene, and being greatest in nitrobenzene. The influence of the benzene nucleus is clearly evidenced by the higher value for benzyl alcohol as compared with the aliphatic alcohols.

In the third column are given the values for k as found, whilst in column four we give these values corrected for the alteration which takes place in the active ester on keeping. This correction was made by subtracting the initial from the final constant in ethyl tartrate alone ($1·85 - 1·745 = 0·105$), and assuming that one-eighth of this increment took place between each of the experiments of the series; thus in the case of *n*-propyl alcohol, which was the third to be used, the tartrate would have become more rapid by $3 \times 0·013 = 0·039$, so that its constant would be 1·784, instead of the original 1·745, and calculating back to the latter value we have $1·725 \times 1·745/1·784 = 1·687$ as the true value of the constant for *n*-propyl alcohol referred to ethyl tartrate, the constant of which undiluted is 1·745. In the fifth column the numbers for the aromatic hydrocarbons are calculated in a similar manner with reference to an ethyl tartrate of constant 1·745 instead of 0·563, so that all the numbers in this column are directly comparable.

In table X are shown, in comparison with our own, the results of other workers so far as is possible. Columns 2, 3, and 4 represent respectively the data given by Menschutkin for the reaction between acetic anhydride and *sec.*-propyl alcohol at 100°, for the reaction between acetic anhydride and *iso*butyl alcohol, and for the combination of triethylamine with ethyl iodide. Columns 5 and 6 contain the data given by Dimroth for the conversion of the enol, methyl 5-hydroxy-1-phenyl-1:2:3-triazole-4-carboxylate (*Annalen*, 1904, **335**, 7), into methyl anilidodiazomalonate (*Annalen*, 1910, **373**, 344) at two different temperatures. Column 7 shows the velocity constants obtained by Tubandt for the inversion of menthone. Column 8 gives v. Halban's numbers for the rate of decomposition of triethylsulphine bromide, whilst the last contains our own results. The numbers given are, in all cases except our own, relative, not actual, constants, whereas with regard to our data, since the value for *iso*butyl alcohol is almost unity, and this is the smallest, the numbers given are practically identical with

TABLE X.

	Menschutkin.			Dimroth.		Tubandt.	v. Halban.	Patterson and Montgomerie.
	Acetic anhydride and		Triethylamine and ethyl iodide. 100†.	Isomerism of a triazole derivative.		Inversion of Menthone.	Decomposition of triethylsulphine bromide.	Anis-*syn*- into anis-*anti*-oxime.
Solvent.	*sec.*-Propyl alcohol. 100°*.	*iso*Butyl alcohol. 100°*.		25°‡.	10°§.	20°.‖	70°.¶	26°.
Water	—	—	—	0·0043	—	—	—	8·26
Methyl alcohol	—	—	286·6	1·00	1·00	1·00	1·0	2·07
Ethyl alcohol.........	—	—	203·3	1·92	1·94	2·60	1·0 [?]	1·86
n-Propyl alcohol ...	—	—	—	—	—	3·38	1·8	1·69
n-Butyl alcohol	—	—	—	—	—	4·10	—	—
*iso*Butyl alcohol......	—	—	143·3	—	—	4·64	—	0·96
Amyl alcohol	—	—	—	—	—	—	—	—
Allyl alcohol	—	—	240·5	—	—	0·63	—	1·56
Benzyl alcohol	—	—	742·2	—	2·08	0·37	—	3·14
Benzene	1·00	1·00	38·2	—	—	—	—	3·13
Toluene	—	—	—	—	—	—	—	2·33
o-Xylene	—	—	—	—	—	—	—	2·19
m-Xylene	1·25 **	1·37 **	15·9	—	—	—	—	2·34
p-Xylene	—	—	—	—	—	—	—	2·44
Mesitylene	—	—	—	—	—	—	—	2·13
Nitrobenzene	—	—	—	—	86·80	—	180·0	2·94
Hexane	2·07	2·18	1·0	—	—	—	—	—
Acetone	—	—	337·7	9·94	9·94	—	290·0	—
Ether	—	—	—	24·50	—	—	—	—
Chloroform............	—	—	—	50·90	39·80	—	230·0	—
n-Butyl alcohol [25°]	—	—	—	—	—	1·00	—	—
*iso*Butyl alcohol ,,	—	—	—	—	—	1·14	—	—
sec.-Butyl alcohol ,,	—	—	—	—	—	2·44	—	—
tert.-Butyl alcohol ,,	—	—	—	—	—	5·48	—	—

* *Zeitsch. physikal. Chem.*, 1887, **1**, 629.

† *Zeitsch. physikal. Chem.*, 1890, **6**, 41.

‡ *Annalen*, 1904, **335**, 7; see also Dimroth (*Annalen*, 1910, **373**, 368) for constants at 50°, in methyl and ethyl alcohol, acetone, and chloroform, for the changes of methyl hydroxybenzyltriazolecarboxylate into the benzylamide of methyl diazomalonate.

§ *Annalen*, 1910, **377**, 131.

‖ *Annalen*, 1907, **354**, 259.

¶ *Zeitsch. physikal. Chem.*, 1909, **7**, 129.

** Menschutkin does not state which xylene was used.

those which would be found by referring the data to the constant for *iso*butyl alcohol as unity.

On the whole, the data thus obtained by very different processes for reactions varying greatly in type, show some remarkable regularities. Menschutkin in his first experiments found that the reaction between acetic anhydride and *n*-propyl alcohol and acetic anhydride and *iso*butyl alcohol were both influenced in much the same way by the solvents benzene, xylene, and hexane, being slowest in the first- and fastest in the last-named. In his next investigation he examined the reaction between triethylamine and ethyl iodide, finding it to be influenced by the solvents mentioned in just the opposite order, being slowest in hexane and quickest in benzene, the effect of the solvent being also very much more marked. His investigation extended to other solvents, some of which are included in the table, when it was found that the velocity was still greater in the monatomic saturated alcohols, very rapid in acetone, and most rapid in benzyl alcohol, being over seven hundred times as fast as in hexane and nearly twenty times as fast as in benzene. The velocity becomes less as the homologous series of alcohols is ascended, and it will be noticed that in our experiments the same is the case. The closeness of the similarity between Menschutkin's results and ours will, however, be better seen from table XI, in which the former are referred to the constant for *iso*butyl alcohol as unity.

TABLE XI.

Solvent.	Menschutkin.	Patterson and Montgomerie.
iso-Butyl alcohol	1·0	0·96
Ethyl ,, ...	1·42	1·86
Allyl ,, ...	1·68	1·56
Methyl ,, ...	2·0	2·07
Benzyl ,, ...	5·18	3·14

It will be observed that the sequence in these alcohols is the same, except in regard to the positions of ethyl and allyl alcohol, Menschutkin's reaction proceeding more rapidly in allyl alcohol, whilst we found the reverse to be the case. Apart from this, the numbers found are strikingly alike, not merely in sequence, but even in magnitude.

Comparing Menschutkin's results and ours for aromatic solvents, there is at once a resemblance and a difference. Menschutkin found that in benzene and xylene triethylamine combines much less rapidly with ethyl iodide than in the alcohols mentioned, whilst we find that, on the whole, the oxime transformation takes place distinctly more rapidly in the benzene series of solvents than in the open-chain alcohols. The sequence, however, is again the same, both reactions proceeding more slowly in xylene than in benzene, the difference being much greater in his case than in ours. It is difficult to account for the position occupied by benzyl alcohol in Menschutkin's table. It might be expected that if benzene itself has so considerable a retarding influence, the introduction of the C_6H_5-group into carbinol would bring about a diminution instead of an increase. Our result for benzyl alcohol seems to be in better agreement with the behaviour of benzene and methyl alcohol. It will be noticed that our constant for toluene is a little lower than that for *m*-xylene; this, we think, is due to slight over-correction, the experiments with this solvent having been done out of their proper order. The constant for benzene is greater than that for toluene, that for toluene is almost certainly greater than that for *m*-xylene, whilst that for *m*-xylene is in turn greater than that for mesitylene.

Our results for the xylenes are, so far as we are aware, the first from which it is possible to compare the relative effects of *o*-, *m*-, and *p*-substitution. The effect is quite marked; the reaction proceeds most rapidly in *p*-xylene, and most slowly in *o*-xylene. It is perhaps worthy of remark that *m*-nitrobenz*syn*aldoxime transforms into the *anti*-form more rapidly than does *o*-nitrobenz*syn*-aldoxime (Patterson and McMillan, *Proc. Roy. Phil. Soc. Glasgow*, 1910–11, **42**, 29).

Turning now to the other columns of table X, several points may be noticed. In the first place, it will be observed that the sequence is the same for Dimroth's transformation, for the inversion of menthone, and for the decomposition of triethylsulphine bromide, but this sequence is just the opposite of that found by Menschutkin and ourselves; the velocity of reaction increases as the homologous series of alcohols is ascended, and in somewhat the same manner in each case; thus the inversion of menthone takes place 2·6 times as rapidly, whilst Dimroth's transformation proceeds about twice as rapidly, in ethyl as in methyl alcohol. The results of v. Halban are of a similar kind.

Again, it may be noticed that whilst Dimroth's reaction takes place very much more slowly, ours takes place much more rapidly in water than in methyl alcohol, so that there is here a distinct agreement at least of a qualitative character.

Any definite effect due to the presence of a double bond is scarcely to be discerned. We find for allyl alcohol a constant, 1·56, very close to that for *n*-propyl alcohol, 1·69; Menschutkin's constant falls between those for methyl and ethyl alcohol, whilst Tubandt's is distinctly lower than that for methyl alcohol.

Our data are insufficient to allow of any definite statement regarding the effect of isomerism in the aliphatic series, but from analogy to the constants for methyl alcohol, 2·07, ethyl alcohol, 1·86, and *n*-propyl alcohol, 1·69, it seems probable that the constant for *n*-butyl alcohol would be about 1·5, distinctly greater than that found for *iso*butyl alcohol, 0·96. Branching in the carbon chain will therefore probably be found to lower the rate of the reaction. Tubandt examined this point more thoroughly, and observed that the constant for his reaction increases from *n*-butyl, through *iso*-

and *sec.*-, to *tert.*-butyl alcohol, and since his reaction is influenced, in other solvents, in just the opposite way from ours, this is in agreement with the conclusion we arrive at from our experiments.

We may also refer to the fact that the range through which our velocity constant varies is smaller than for the other investigations quoted. It must be remembered, however, that in Menschutkin's experiments, for example, one volume of reaction mixture was diluted with fifteen volumes of the solvent, whilst in ours, one volume of reaction mixture was diluted with only one-third of a volume of the solvent, and if it be permissible to assume that the effect of the solvent will bear a fairly direct relationship to its quantity, then the range of our constants would probably be considerably increased in the presence of a larger proportion of solvent. That the effect of so small a proportion of solvent can be detected thus clearly is a sign of its great importance.

Some other investigations which cannot be summarised in table X, may be briefly referred to. Walker and Kay (Trans., 1897, **71**, 504) found that the velocity of transformation of ammonium cyanate into carbamide is very greatly accelerated by the addition of ethyl alcohol, the value of the constant for 90 per cent. alcohol being nearly one hundred times as great as the value for pure water, and this in spite of a co-existent retardation which the alcohol effects by diminishing the number of active molecules present in the solution. Other neutral substances were found to exert a similar accelerating influence in the following order of increasing rapidity: glycerol, ethyl alcohol, sucrose, glycol, methyl alcohol, acetone. Lowry (Trans., 1899, **75**, 211) followed the mutarotation of nitrocamphor in various solvents; Lowry and Robertson (Trans., 1904, **85**, 1548) found that β-bromo-ψ-nitrocamphor apparently passes much more rapidly in benzene solution than in chloroform solution into its stable form; Lowry and Magson (Trans., 1908, **93**, 110) give for the change of nitrocamphor into ψ-nitrocamphor the following velocity constants: in ethyl alcohol, 0·0048; acetic acid, 0·0025; ether, 0·00149; and in benzene, 0·00013. Dawson and Miss Leslie, studying the reaction between acetone and iodine, assume, with Lapworth (Trans., 1904, **85**, 30), that the acetone before being acted on by the iodine, undergoes a tautomeric change into the enolic form, and they have measured the velocity of this change in various solvents. They find that it is greatest in methyl alcohol, diminishing successively in nitrobenzene, benzene, carbon tetrachloride, whilst in water the velocity is, relatively, nil; although these data are perhaps rather scanty, it may nevertheless be noticed that the sequence—methyl alcohol, nitrobenzene, benzene —is the same as that found by us, except that in the former case the above order is one of diminishing velocity, whereas in the latter it is that of increasing velocity. The position of water, however, as Dawson and Miss Leslie remark, does not seem to be in harmony with their other results. Again, it may be mentioned that Klein (*J. Physical Chem.*, 1911, **15**, 1) finds the reaction between hydrogen sulphide and sulphur dioxide to take place readily in alcoholic solution, whilst it does not appear to occur at all in benzene.

In general, therefore, reviewing the experiments which have been quoted and some others to which no reference has been made, it appears that solvents influence quite different reactions in a uniform manner, although the manifestation of this effect may be of an opposite character; a given set of solvents may hasten a particular reaction in a certain sequence, whilst in the same or very nearly the same sequence they retard another reaction. The property or properties of the solvents which bring this about are probably the same throughout, just as, in a similar manner, a given force may accelerate the velocity of a body moving in one direction, whilst it will retard the motion of a body moving in the opposite direction. The apparently opposite effects are manifestations of the same cause. Although other investigators have discussed some of the phenomena we have referred to, with a view to exhibiting a relationship between the magnitude of the velocity constants and the dielectric constant of the solvents, without any marked success, we nevertheless think that the character of the results generally is such as indicates a physical cause for the influence of the solvent. The most recent correlation of this character has been made by Dimroth, who adopts a suggestion of van't Hoff connecting the velocity of transformation of a labile substance in various media with its solubility in these media. That the application of this interesting idea is likely to be attended with difficulty must be clear from the fact, amongst others, that one chemical individual may have several different solubilities in the same liquid, the solubility being a function of the state of aggregation of the solute. If, however, the maximum solubility—that, presumably, of the liquid solute—were chosen, the difficulty referred to might, to some extent, disappear.* It is, at least, certain that the solubilities found by Dimroth, which probably, from the method of determination, are really those of the liquid solute, show a remarkable relationship to the values found for the velocity constant (*Annalen*, 1910, **377**, 131). The rate of transformation of the *aci*-form becomes greater as its solubility diminishes. This suggestion has also been considered in the case of the tautomerism of acetoacetic ester by K. H. Meyer (*Annalen*, 1911, **380**, 229).

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* Mutually miscible liquids present an obvious difficulty.

The idea of complex formation has been less readily accepted in this than in some other fields, and it might, we consider, be expected that, if these effects were due to complex formation, the influence of each solvent on each reaction would probably be specific, in which case the general results ought to be quite erratic. The suggestion of hydrogen ion catalysis has also been made, but has met with no success.

Whether all reactions are catalysed or not, the one we have examined certainly is, although we have not yet found an opportunity to investigate the nature of the catalyst. Since, however, it has been shown by Tubandt (*Annalen*, 1911, **377**, 284) that the influence of solvents on the velocity of inversion of menthone may differ to some extent according to the catalyst used, this might prove to be the case with our reaction also, and we were afraid, in commencing our work, that solvents purified without any very special precautions might perhaps contain small quantities of foreign substances which would catalyse the oxime transformation erratically. This, however, does not appear to be the case, more especially since Dunstan and Mussell (this vol., p. 571) were unable to bring about the transformation of the oximes at all, even at relatively high temperatures, in water, ethyl alcohol, benzene, and amyl acetate.

Unfortunately, our collaboration was brought to an end sooner than we had expected and before the programme we had arranged was completed, but we hope to have a future opportunity of carrying our work a stage further.

In conclusion, we wish to express our thanks to the Carnegie Trustees for the Universities of Scotland, who kindly placed at the disposal of one of us the large polarimeter with which this research was carried out.

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III.—*The Velocity of Interaction of Iodic and Sulphurous Acids in Various Media.*

By Thomas Stewart Patterson and William Collins Forsyth.

In connexion with the experiments detailed in the preceding paper, we thought it would be of interest to examine some other type of reaction, and chose, as one perhaps allowing of very simple observation, the well known experiment of Landolt on the reduction of iodic acid by sulphurous acid (*Ber.*, 1886, **19**, 1340; 1887, **20**, 745). Dilute solutions of these reagents are mixed, a small quantity of starch solution being present, and after the lapse of a definite time, depending on the concentration of the solutions and the temperature, a blue colour suddenly appears, due to the action of the liberated iodine on the starch. Landolt himself made some experiments regarding the influence of added inactive substances, and found that acids—sulphuric, hydrochloric, oxalic, acetic—hasten the reaction the more the greater is the affinity constant of the acid. Sodium chloride and ammonium chloride were also found to accelerate the reaction, but to a less extent. Similarly, alcohol in the proportion of 7 to 3 of water in the solution reduced the time necessary for the appearance of the blue colour from 102·2 secs. to 90·4 secs. He says that the influence of alcohol is thus not great, and that he was unable to find a liquid which definitely retarded the velocity of the reaction.

For the following experiments our reagents were made as follows: Of a saturated solution of sulphur dioxide, 50 c.c. were diluted to a litre, whilst 10 grams of iodic acid were dissolved in 1 litre of water. For an experiment, 10 c.c. of sulphur dioxide solution were first mixed with 2 c.c. starch solution, and to this were added 100 c.c. of diluent, water, for example. To this mixture 10 c.c. of iodic acid solution were quickly added, the temperature being about 20° in all cases. In the above instance the blue colour flashed out in nineteen seconds. In other experiments, instead of the 100 c.c. of water, 100 c.c. of pure methyl, ethyl, *n*-propyl alcohol, or acetone, or mixtures of these with water in known proportions were added. The colour which appeared in the solution was blue or yellow, according to the proportion of neutral solvent added.

In the case of methyl alcohol the following results were obtained:

Percentage of methyl alcohol in 100 c.c. of added diluent.	Time.
0	19 seconds
50	9 ,,
100	2 ,,

It thus appears that the addition of methyl alcohol hastens this reaction very considerably, and practically in direct proportion to the quantity of alcohol added. It was then found that ethyl and *n*-propyl alcohol behaved in a manner quite similar to methyl alcohol, the accuracy of the method of investigation being insufficient to detect any distinct variation.

On the addition of acetone the results were somewhat different, as the following table shows:

Percentage of acetone in 100 c.c. of added diluent.	Time.
0	19 seconds
25	23 ,,
50	24 ,,
60	20 ,,
75	15 ,,
100	3 ,,

The velocity of the reaction increases at first as the proportion of acetone increases up to about 50 per cent., to diminish again rapidly thereafter.

It is not possible much to extend the examination of this reaction, since the solvents used must (1) be neutral or acid, and (2) be miscible with water, two conditions which considerably limit the number of available liquids. In addition, although the reaction is one which can be timed fairly accurately, the variation in colour of the starch iodide and also the complexity of the whole reaction render the results at least difficult of interpretation.

We need only remark that an increase in the velocity of a reaction, on the addition of a neutral solvent, to reach a maximum has been observed in numerous cases; thus, Dawson (Trans., 1911, **99**, 1) found the reaction between iodine and acetone with a little sulphuric acid in presence of ethyl alcohol to be very greatly reduced by the addition of small quantities of water, whilst Tubandt (*Annalen*, 1907, **354**, 259) has recorded a somewhat similar observation in regard to the inversion of menthone. For other references Dawson's paper should be consulted.

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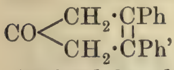
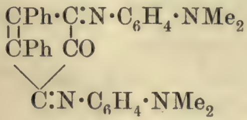
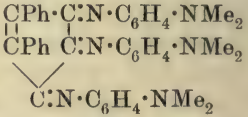
IV.—*Diphenyl*cyclo*pentenone.*

By Siegfried Ruhemann and William Johnson Smith Naunton.

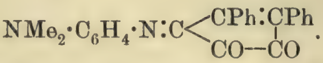
The study of the cyclic ketonic compounds, in which one of us has been engaged for some time, led to the knowledge of triketohydrindene, the first member of the cyclic triketones containing three adjacent ketonic groups in an *iso*cyclic system. This compound appears to be of especial interest on account of its close resemblance to alloxan and of its characteristic colour reactions with proteins and their hydrolytic products.

With the view of preparing similar substances and examining their behaviour, we have subjected 3:4-diphenyl*cyclo*pentenone,  $CO<\begin{smallmatrix}CH_2\cdot CPh\\ \|\\ CH_2\cdot CPh\end{smallmatrix}$, which Japp and Burton (Trans., 1887, **51**, 420) obtained by the action of hydriodic acid on anhydroacetonebenzil, to the same treatment as the mono- and di-ketones of hydrindene. On applying Sachs and Barschall's method of transforming methylene groups into ketonic groups (*Ber.*, 1901, **34**, 3047), it was found that *p*-nitrosodimethylaniline reacts with the *cyclo*pentenone mainly to form 2:5-*bis-dimethylaminoanilo*-3:4-*diphenyl*cyclo*pentenone* (I), but at the same time a compound is produced, the analytical results of which point to a compound of the formula (II).


(I.),

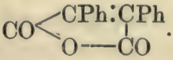

(II.)

Its formation is to be explained by the assumption of the partial reduction of the former compound, and its subsequent condensation with another molecule of *p*-nitrosodimethylaniline. This constitution is supported by its behaviour towards mineral acids, since both substances yield 5-*dimethylaminoanilo*-3:4-*diphenyl*cyclo*pentene*-1:2-*dione*:

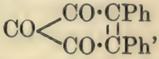


$$NMe_2\cdot C_6H_4\cdot N{:}C<\begin{smallmatrix}CPh{:}CPh\\ |\\ CO{-}CO\end{smallmatrix}.$$

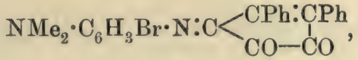
The fact that, under the influence of acids, the groups $:N\cdot C_6H_4\cdot NMe_2$ are removed with the exception of one of them, is most remarkable in view of the observations of Sachs and his collaborators, and of the fact that bis-dimethylaminoanilo-α-hydrindone on treatment with acids readily yields triketohydrindene hydrate (Trans., 1910, **97**, 1438). The stability of 5-dimethylaminoanilo-3:4-diphenyl*cyclo*pentene-1:2-dione is, in fact, so great that the removal of the group $\vdots\mathrm{N{\cdot}C_6H_4{\cdot}NMe_2}$ could not be accomplished without effecting at the same time a deep-seated change to diphenylmaleic anhydride:



$$\mathrm{CO}<\begin{array}{l}\mathrm{CPh{:}CPh}\\ \mathrm{O{-}{-}{-}CO}\end{array}.$$

This transformation takes place very slowly and incompletely on boiling the compound with potassium hydroxide or hydrochloric acid under the ordinary pressure, but more readily on heating with concentrated hydrochloric acid at 130—140° for several hours. The change of 5-dimethylaminoanilo-3:4-diphenyl*cyclo*pentene-1:2-dione into 4:5-diphenyl*cyclo*pentene-1:2:3-trione,  $\mathrm{CO}<\begin{array}{l}\mathrm{CO{\cdot}CPh}\\ \mathrm{CO{\cdot}CPh}\end{array}$, cannot be effected by means of either nitric acid or bromine. These reagents mainly yield substitution products.

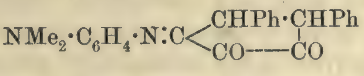
With fuming nitric acid it forms a deep red *dinitro*-derivative, $\mathrm{C_{25}H_{18}O_2N_2(NO_2)_2}$, whereas bromine reacts with the compound to form a yellow *monobromo*-derivative, $\mathrm{C_{25}H_{19}O_2N_2Br}$, when the reagents are used in molecular proportions. From the fact that this bromo-substitution product, on heating with concentrated hydrochloric acid, yields diphenylmaleic anhydride, it follows that substitution has taken place in the benzene nucleus of the dimethylaminoanilo-group, and that therefore its constitution is to be represented thus:



$$\mathrm{NMe_2{\cdot}C_6H_3Br{\cdot}N{:}C}<\begin{array}{l}\mathrm{CPh{:}CPh}\\ \mathrm{CO{-}CO}\end{array},$$

in which only the orientation of the bromine atom is doubtful. On using, however, two molecules of the halogen to one molecule of the substance, a yellow, crystalline compound is obtained, which loses halogen even on drying in the air. This substance is undoubtedly the perbromide of a bromo-substitution product of the azomethine. On boiling with alcohol, this perbromide decomposes, and yields besides the former yellow monobromo-substitution product, a deep red *dibromo*-derivative of the azomethine.

The red solution of the compound, $\mathrm{C_{25}H_{20}O_2N_2}$, in glacial acetic acid is readily decolorised by zinc dust to yield a colourless base, $\mathrm{C_{25}H_{22}O_2N_2}$, which is to be regarded as 5-*dimethylaminoanilo*-3:4-*diphenyl*cyclo*pentane*-1:2-*dione*:



$$\mathrm{NMe_2{\cdot}C_6H_4{\cdot}N{:}C}<\begin{array}{l}\mathrm{CHPh{\cdot}CHPh}\\ \mathrm{CO{-}{-}{-}CO}\end{array}.$$

This constitution follows from the fact that the substance on heating with concentrated hydrochloric acid decomposes to form *s*-diphenylsuccinic acid.

The azomethine, $\mathrm{C_{25}H_{20}O_2N_2}$, is orange or red, and has basic properties, forming salts with acids, which, with the exception of the platinic salt, are readily dissociated by water. The compound is practically insoluble in cold alcohol, but on boiling it dissolves sparingly, and on cooling small, deep red plates separate from the concentrated solutions, whereas it crystallises from more dilute solutions in absolute alcohol in orange needles. If a little water is added to the hot alcoholic solution of the compound, no crystals separate on cooling, but the whole sets to a transparent jelly, which according to the concentration is yellow or yellowish-red. This gel, when kept at the ordinary temperature, gradually liquefies, and in the course of one to two days completely disappears, with separation from the resulting solution of the azomethine in orange needles. The transformation of the substance into the colloidal state occurs with solvents which are miscible with water, and therefore takes place with acetone, but it is not observed in solvents like chloroform or benzene, which are immiscible with water. It is probable that this phenomenon is accompanied by the formation of a hydrate, which spontaneously loses water and yields the original compound. This exceptional property of the azomethine, which is not to be found with its bromo- or nitro-substitution products, will be subjected to a closer study.

EXPERIMENTAL.

Action of p-*Nitrosodimethylaniline on* 3:4-*Diphenyl*cyclo*pentenone.*

The *cyclo*pentenone was prepared from anhydroacetonebenzil according to the directions of Japp and Lander (Trans., 1897, **71**, 131), with the difference that the product which is obtained on the reduction of anhydroacetonebenzil was twice recrystallised from alcohol with the use of animal charcoal, instead of distilling under diminished pressure, as stated by these authors. The compound was obtained in colourless needles melting at 110°. On treatment with *p*-nitrosodimethylaniline it was found that two condensation products are produced, which contain two and three dimethylaminoanilo-groups respectively, even when the reagents are used in the proportion of one molecule of the pentenone to two molecules of the nitroso-derivative. On account of this fact an excess of the nitroso-compound was used, and the reaction was carried out as follows: The pentenone (5 grams) and *p*-nitrosodimethylaniline (10—12 grams), dissolved in hot alcohol, are mixed, and a little concentrated alcoholic potassium hydroxide is gradually added to the cold solution of the mixture. The green colour of the solution changes to brown, and a dark solid separates, which increases in quantity in the course of three to four days. To remove impurities it is boiled with alcohol, in which it is only sparingly soluble, and dried in the steam-oven; the product dissolves in hot chloroform to yield a dark red solution, and on cooling partly crystallises in brown needles, whereas the other part does not separate until the solution is considerably concentrated or mixed with alcohol. The substance which is less soluble in chloroform melts at 255°, but on repeated crystallisation from the same solvent it is obtained in chocolate-coloured needles, which melt at 265° after softening a few degrees before:

0·2031 gave 0·5855 CO_2 and 0·1190 H_2O. C = 78·62; H = 6·51.
0·2012 „ 0·5807 CO_2 „ 0·1175 H_2O. C = 78·71; H = 6·49.
0·2021 „ 24·5 c.c. N_2 at 21° and 755 mm. N = 13·67.
$C_{41}H_{40}N_6$ requires C = 79·87; H = 6·49; N = 13·63 per cent.

The substance appears to be 1:2:3-*tris-dimethylaminoanilo*-4:5-*diphenyl*cyclo*pentene* (II, p. 42).

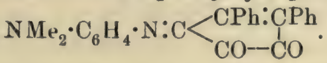
The deficit in the percentage of carbon is probably due to a small quantity of impurity, although after more frequent recrystallisation results were obtained on analysis which do not materially differ from those given above.

The purification of the main product of the action of *p*-nitrosodimethylaniline on diphenyl*cyclo*pentenone, which product is contained in the mother liquor of the former condensation product, can be readily accomplished. It separates on distilling the larger portion of the chloroform and adding alcohol to the hot concentrated solution until crystallisation commences. If the substance is twice recrystallised from a mixture of chloroform and alcohol, it is obtained in bronze needles, which melt at 211—212°:

0·1760 gave 0·5125 CO_2 and 0·0965 H_2O. C = 79·42; H = 6·09.
0·1633 „ 15·8 c.c. N_2 at 19° and 775 mm. N = 11·34.
$C_{30}H_{30}ON_4$ requires C = 79·51; H = 6·02; N = 11·24 per cent.

This compound is 2:5-*bis-dimethylaminoanilo*-3:4-*diphenyl*cyclo*pentenone* (I, p. 42).

5-*Dimethylaminoanilo*-3:4-*diphenyl*cyclo*pentene*-1:2-*dione*,



$$NMe_2\cdot C_6H_4\cdot N\colon C<\begin{matrix}CPh\colon CPh\\ \quad\;\; | \\ CO-CO\end{matrix}.$$

Both substances which are formed by the condensation of *p*-nitrosodimethylaniline with the *cyclo*pentenone show the same behaviour; they have basic properties, and dissolve in cold hydrochloric or sulphuric acids to yield deep red solutions, which gradually at the ordinary temperature, but rapidly on warming on the water-bath, become turbid; a yellow, tenacious, and elastic product separates, which in the course of a day sets to a hard, brittle mass, turning red on washing with water. This substance dissolves in boiling absolute alcohol, and on cooling crystallises in orange needles, melting at 191—192°:

0·1681 gave 0·4865 CO_2 and 0·0790 H_2O. C=78·93; H=5·22.
0·1733 „ 11·4 c.c. N_2 at 23° and 764 mm. N=7·45.
$C_{25}H_{20}O_2N_2$ requires C=78·95; H=5·26; N=7·37 per cent.

5-*Dimethylaminoanilo*-3:4-*diphenyl*cyclo*pentene*-1:2-*dione* is sparingly soluble in ether, almost insoluble in cold alcohol; it dissolves sparingly in boiling alcohol, 1 gram of the substance requiring 110 c.c. of boiling alcohol; from this solution the compound separates in small, deep red plates as compared with the orange needles, in which it crystallises from less concentrated solutions in absolute alcohol. It has been mentioned above (p. 44) that the behaviour of the substance is quite different if water is added even to the dilute solution in absolute alcohol; on cooling in this case no crystals separate, but the whole sets to a transparent jelly, which gradually liquefies, and at the same time deposits orange needles of the original compound. The same phenomenon occurs if acetone is used as a solvent instead of alcohol. The compound, $C_{25}H_{20}O_2N_2$, is very soluble in benzene or chloroform, but the red solutions which are formed do not gelatinise on the addition of water.

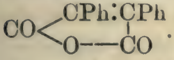
The azomethine has basic properties, forming salts with acids, which, however, are dissociated by water. On the addition of hydrochloric acid it turns yellow, and yields a gelatinous hydrochloride identical with the salt which is formed in the preparation of the azomethine from the condensation-products of diphenyl*cyclo*pentenone with *p*-nitrosodimethylaniline. The hydrochloride gradually solidifies to a brittle mass, which on washing with water loses hydrogen chloride and turns orange. The hydrochloride readily dissolves in alcohol to yield a yellow solution, which on treatment with platinum chloride forms a *platinichloride*, separating in bunches of yellow needles; they soften at 232°, and melt and decompose at 236°:

0·3055 gave 0·0509 Pt. Pt=16·66.
$(C_{25}H_{20}O_2N_2)_2,H_2PtCl_6$ requires Pt=16·68 per cent.

The orange substance, $C_{25}H_{20}O_2N_2$, also forms a yellow sulphate, which is readily decomposed by water into base and acid.

Formation of Diphenylmaleic Anhydride from 5-Dimethylaminoanilo-3:4-*diphenyl*cyclo*pentene*-1:2-*dione.*

The compound, $C_{25}H_{20}O_2N_2$, on boiling with concentrated aqueous potassium hydroxide or with hydrochloric acid under the ordinary pressure is only slightly attacked, but when heated with concentrated acid in a sealed tube to 130—140° for four hours it is transformed into a pale yellow solid. This is collected, washed with water, and digested with dilute potassium hydroxide, when it almost completely dissolves. On adding hydrochloric acid to the alkaline filtrate a flocculent substance is precipitated, which readily dissolves in hot alcohol, and crystallises from dilute alcohol in faintly yellow needles, melting at 156—157°. The melting point and the properties characterise this compound as diphenylmaleic anhydride,



$\mathrm{CO}<\begin{array}{l}\mathrm{CPh{:}CPh}\\ \mathrm{O{-}{-}CO}\end{array}$.

Its composition has been verified by analysis. (Found, $C=76{\cdot}85$; $H=4{\cdot}01$. Calc., $C=76{\cdot}80$; $H=4{\cdot}00$ per cent.) The action of hydrochloric acid on the azomethine, therefore, not only effects the replacement of the group $:N{\cdot}C_6H_4{\cdot}NMe_2$ by oxygen, but at the same time the removal of the adjacent ketonic group. All attempts to produce 4:5-diphenyl*cyclo*pentene-1:2:3-trione (p. 43) or its hydrate from the compound $C_{25}H_{20}O_2N_2$ have been unsuccessful.

Action of Bromine and Nitric Acid on the Compound $C_{25}H_{20}O_2N_2$.

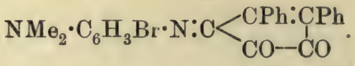
By the action of these reagents the removal of the group $:N{\cdot}C_6H_4{\cdot}NMe_2$ does not take place, but substitution products are formed instead. If bromine (1 gram) is gradually added to the solution of the azomethine (2·3 grams) in chloroform, the halogen rapidly disappears, the colour of the solution becomes yellow, and no precipitate is formed if the reagents are used in exact equimolecular proportions. On mixing the chloroform solution with light petroleum a yellow solid is precipitated, which dissolves in much boiling alcohol, and on cooling slowly crystallises in long, yellow prisms, which soften at about 152°, and melt at 154° to a red liquid:

0·2017 gave 0·4828 CO_2 and 0·0770 H_2O. $C=65{\cdot}28$; $H=4{\cdot}24$.
0·2545 „ 0·1038 AgBr. $Br=17{\cdot}35$.
$C_{25}H_{19}O_2N_2Br$ requires $C=65{\cdot}36$; $H=4{\cdot}14$; $Br=17{\cdot}43$ per cent.

The bromo-derivative is sparingly soluble in ether or cold alcohol. With mineral acids it forms salts, which are readily dissociated by water. The hydrochloride dissolves in warm alcohol, and the cold yellow solution on the addition of platinic chloride yields a *platinichloride*, which gradually separates in yellow needles, softening at 189° and melting at 195°:

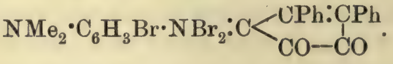
0·2730 gave 0·0395 Pt. $Pt=14{\cdot}47$.
$(C_{25}H_{19}O_2N_2Br)_2,H_2PtCl_6$ requires $Pt=14{\cdot}67$ per cent.

The bromo-derivative, which does not show the phenomenon of being transformed into the colloidal state, on heating with concentrated hydrochloric acid in a closed tube at 135—140° for about five hours, suffers a similar decomposition to the azomethine, $C_{25}H_{20}O_2N_2$. An almost colourless solid is formed, which dissolves in hot dilute potassium hydroxide, and is precipitated from the alkaline solution on the addition of hydrochloric acid. The substance crystallises from dilute alcohol in pale yellow prisms, which are free from halogen and melt at 156—157°. These properties characterise it as diphenylmaleic anhydride. Its formation leads to the conclusion that the bromine has entered into the benzene nucleus of the dimethylaminoanilo-group of the azomethine, and that, therefore, the bromo-derivative has the formula:



$$NMe_2\cdot C_6H_3Br\cdot N{:}C{<}\begin{matrix}CPh{:}CPh \\ CO{-}CO\end{matrix}.$$

Quite different, however, is the action of bromine on the azomethine, $C_{25}H_{20}O_2N_2$, if two molecules of halogen are slowly added to a solution of one molecule of the compound in chloroform; in this case a precipitate consisting of bunches of yellow needles is produced. This product, which is very sparingly soluble in chloroform, is very unstable, since it constantly loses bromine in a vacuum desiccator or even on drying in the air. This behaviour, which points to the view that the substance is a perbromide, prevented us from fixing its composition by analysis, but the decomposition which it suffers on boiling with alcohol, in which it yields a mixture of the mono- and dibromo-derivatives of the azomethine, indicates that it is the perbromide of the yellow monobromo-compound, $C_{25}H_{19}O_2N_2Br$, and that, therefore, it is probably represented by the formula:



$$NMe_2\cdot C_6H_3Br\cdot NBr_2{:}C{<}\begin{matrix}CPh{:}CPh \\ CO{-}CO\end{matrix}.$$

The perbromide dissolves in much boiling alcohol to yield a yellow solution, from which, on cooling, red needles separate; these, however, do not represent a pure substance, but a mixture of the yellow bromo-compound, $C_{25}H_{19}O_2N_2Br$, and a red dibromo-derivative of the azomethine. Owing to the fact that the dibromo-compound is less soluble than the monobromo-derivative, the isolation of the former can be effected by recrystallisation from boiling alcohol. After repeating the process of purification three times, the *dibromo*-derivative is obtained in long, scarlet needles, which soften at 212°, and melt at 214°:

0·2076 gave 0·4262 CO_2 and 0·0625 H_2O. C=55·99; H=3·34.
0·2090 „ 0·1450 AgBr. Br=29·53.
$C_{25}H_{18}O_2N_2Br_2$ requires C=55·76; H=3·34; Br=29·73 per cent.

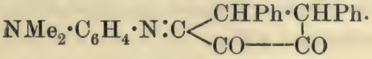
The alcoholic liquor from this compound, on concentration, yielded yellow prisms, which were identified as the monobromo-compound, $C_{25}H_{19}O_2N_2Br$, by the melting point.

Fuming nitric acid readily reacts with the azomethine, $C_{25}H_{20}O_2N_2$. On adding an excess of the acid to the cold solution of the compound in glacial acetic acid, a *dinitro*-derivative, $C_{25}H_{18}O_2N_2(NO_2)_2$, gradually separates. It is sparingly soluble in boiling alcohol, readily so in hot glacial acetic acid, and crystallises in well-defined scarlet prisms, which soften at 220° and melt and decompose at 224°:

0·2027 gave 0·4766 CO_2 and 0·0733 H_2O. C = 64·12; H = 4·01.
0·2254 „ 24 c.c. N_2 at 20° and 759 mm. N = 12·16.
$C_{25}H_{18}O_6N_4$ requires C = 63·83; H = 3·83; N = 11·91 per cent.

The positions of the nitro-groups in this compound have not been ascertained, but judging from the action of bromine on the azomethine, $C_{25}H_{20}O_2N_2$, there can hardly be any doubt that at least one of them is contained in the benzene nucleus of the dimethylaminoanilo-group. Simultaneously with the formation of the dinitro-derivative, there is produced a small amount of diphenylmaleic anhydride, which is contained in the mother liquor of the product of the reaction, and is precipitated on the addition of water. It was purified by dissolving it in warm alkali, and reprecipitating it with acid. After recrystallisation from dilute alcohol, it melted at 156—157°.

5-*Dimethylaminoanilo*-3 : 4-*diphenyl*cyclo*pentane*-1 : 2-*dione*,



$$NMe_2\cdot C_6H_4\cdot N\colon C<\begin{matrix} CHPh\cdot CHPh \\ CO\text{———}CO \end{matrix}$$

As yet only the action of zinc dust on the solution of the azomethine in glacial acetic acid has been examined, with the result that a colourless compound, with the composition $C_{25}H_{22}O_2N_2$, is produced. The red solution of the azomethine (5 grams) in acetic acid is readily decolorised by zinc dust, and on adding water to the filtrate a colourless solid (3·5 grams) is precipitated, which dissolves in much boiling alcohol, and, on cooling, crystallises in colourless needles, melting at 210—211°:

0·2168 gave 0·6255 CO_2 and 0·1155 H_2O. C = 78·68; H = 5·92.
0·1997 „ 13·3 c.c. N_2 at 18° and 742 mm. N = 7·50.
$C_{25}H_{22}O_2N_2$ requires C = 78·53; H = 5·75; N = 7·33 per cent.

The substance has basic properties, forming a hydrochloride which, with platinic chloride, yields a *platinichloride*:

0·2470 gave 0·0393 Pt. Pt = 15·91.
$(C_{25}H_{22}O_2N_2)_2,H_2PtCl_6$ requires Pt = 15·72 per cent.

The base, $C_{25}H_{22}O_2N_2$, on heating with concentrated hydrochloric acid at 130—140° for three hours, decomposes in a manner similar to 5-dimethylaminoanilo-3 : 4-diphenyl*cyclo*pentene-1 : 2-dione to yield *s*-diphenylsuccinic acid. The colourless solid which is produced in this reaction is collected, washed with water, and dissolved in hot dilute alcohol or acetic acid; from these solutions the acid separates in colourless needles or prisms, which melt at 252°. (Found, C=71·18; H=5·30. Calc., C=71·11; H=5·19 per cent.)

This acid is β-diphenylsuccinic acid. The statements as to its melting point differ widely. Reimer (*Ber.*, 1881, **14**, 1803), as well as Chalaney and Knoevenagel (*Ber.*, 1892, **25**, 296), give 229°; Anschütz and Bendix (*Annalen*, 1890, **259**, 61), 245°; whereas Roser (*Annalen*, 1888, **247**, 152) found 252°, which latter statement agrees with our observation. An explanation for these great differences cannot as yet be given. The acid mother liquor from β-*s*-diphenylsuccinic acid, which is formed by the decomposition of dimethylaminoanilodiphenyl*cyclo*pentanedione, also contains, in addition to dimethyl-*p*-phenylenediamine, α-*s*-diphenylsuccinic acid. This was extracted with ether, and after evaporation of the ether was recrystallised from water, in which it is rather soluble. It fuses at 183°, then solidifies, and finally melts at 220—221°; this observation agrees with Reimer's statement (*loc. cit.*).

The behaviour of diphenyl*cyclo*pentenone recorded in this paper is of sufficient interest to merit a closer study. This work is in progress as well as the investigation of other cyclic ketonic compounds on the same lines as those employed in the case of the ketones of the hydrindene series.

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V.—*The Porosity of Iron and its Relation to Passivity and Corrosion.*

By JOHN ALBERT NEWTON FRIEND, D.Sc.

APPARENTLY the earliest attempt to explain passivity was made by Schönbein,* in 1836, who suggested that the inactivity of the iron was caused by the presence of a thin layer of iron oxide covering the surface of the metal. This view was apparently confirmed by the fact that all powerful oxidisers are capable of rendering iron passive, whilst reducing agents readily render the passive metal active. In view of the more recent work of Heathcote (*J. Soc. Chem. Ind.*, 1907, **26**, 899), Krassa (*Zeitsch. Elektrochem.*, 1909, **15**, 490 and 981), Manchot (*Ber.*, 1909, **42**, 3492), and Dunstan and Hill (Trans., 1911, **99**, 1853), there can be no doubt that in many cases this is the correct explanation. Dunstan and Hill have drawn attention to the fact that iron is rendered passive by immersion in alkaline solutions. They do not, however, offer any explanation of the fact, inasmuch as there would appear to be no possibility of the formation of a protective layer of oxide on the surface of the metal.

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* A full account of the passivity of iron with exhaustive references is given in "The Corrosion of Iron and Steel" (Longmans, 1911), Chap. XII, by the present author.

It seemed of importance, therefore, to study more carefully the phenomena of passivity as induced by this method. In the present research the test for passivity was that suggested by Dunstan and Hill, namely, the immersion of the sample of iron in water alongside of, but not actually in contact with, a similar piece of metal known to be active, and observing the times required for pronounced rusting to occur. The active metal always showed clear signs of rust in the course of eight or ten minutes, whereas the passive metal retained its bright surface for much longer periods. These observations coincide entirely with those of Dunstan and Hill.

Series I.—Pieces of Kahlbaum's pure iron foil measuring 4 × 4 cm. in area were cleaned with emery paper and immersed in concentrated solutions of sodium hydroxide (approx. 6*N*) for a period of three weeks. On removal they were thoroughly washed in a stream of distilled water, laid in shallow porcelain dishes, and just covered with a small quantity of distilled water, being shielded from dust and evaporation by glass covers. On applying the usual flame test for sodium with clean platinum wire, no trace of that metal could be detected in the water in the dishes, showing that the iron had been properly washed. After about ten hours a trace of sodium could be detected in solution, and twenty-four hours later the reaction was well marked, the Bunsen flame assuming a bright and persistent yellow colour. Examination with the spectroscope confirmed the presence of sodium. Blank tests simultaneously carried out proved that the sodium could not have dissolved out of the basin itself, nor yet have entered the dish with particles of dust. It must therefore have dissolved out of the iron.

An exactly similar series of experiments was carried out, in which the sodium hydroxide was replaced by an equally strong solution of potassium hydroxide. In this case the potassium could not be distinctly recognised by the flame test within forty-eight hours.

After about sixty hours the reaction was as decided as that for sodium.

From this it would appear that the iron is slightly porous, and the passivity induced by immersion in alkaline solutions is due to the absorption of minute quantities of the alkali. This hypothesis receives confirmation from the following series of experiments.

Series II.—Pieces of pure iron foil which had been immersed for three weeks in concentrated solutions of potassium hydroxide were thoroughly washed with water, dried, and vigorously polished with emery paper. After a second thorough washing they were placed in shallow porcelain dishes with other similar pieces of active foil, and covered with water. Whilst the active metal corroded in eight or ten minutes as usual, the samples that had previously been in the alkali remained bright for several hours, and then slowly began to oxidise. In twenty-four hours no difference between the two sets of specimens was apparent, showing that the passivity had disappeared.

Now all experimenters agree that ordinary passivity is rapidly lost, even on gently handling the metal. Clearly, therefore, a passivity capable of withstanding the vigorous action of emery paper must be of a very different type, and one which is not concerned merely with the surface of the metal. In this case the oxide theory is untenable, the only feasible explanation being that the metal is protected by traces of alkali absorbed into its pores. This further explains why the metal was found to rust in a normal manner after a few hours, for the absorbed alkali would gradually diffuse out of the metal into the water, become neutralised with carbon dioxide, and thus cease to protect the metal.

Series III.—Plates of wrought iron, No. 22 B.W.G., and measuring 14 × 10·5 cm. in area, were treated in the following manner:

Nos. 1 and 2 were cleaned thoroughly with emery paper.

Nos. 3 and 4 were "pickled" for ten hours in dilute sulphuric acid, thoroughly washed with water, dried first with filter paper, and then by warming for ten minutes in a steam-oven.

Nos. 5 and 6 were "pickled" in dilute sulphuric acid for the same period of time as Nos. 3 and 4. They were then thoroughly washed with water, and immersed in 2*N*-sodium hydroxide for one hour. After again washing, they were dried for ten minutes in a steam-oven.

The above six plates were now weighed, and placed in a thermostat, being arranged round the internal circumference of the vessel in a vertical position, as indicated in the figure. Each plate rested on an earthenware beehive, which latter stood on a plate of paraffin wax covering the bottom of the thermostat. The upper parts of the plates leaned against a glass rod bent in the form of a hoop to fit inside the thermostat. These precautions were essential in order to prevent galvanic action from taking place between the several plates. Water was continuously passed into the thermostat through *C*, and on reaching the level *A* was rapidly syphoned off through *B* until its level fell to *D*. In this way the plates were alternately exposed to wet and dry, each refilling of the vessel taking some two hours. After six days the plates were removed, cleaned, dried in the steam-oven, and weighed. The results are given in the following table:

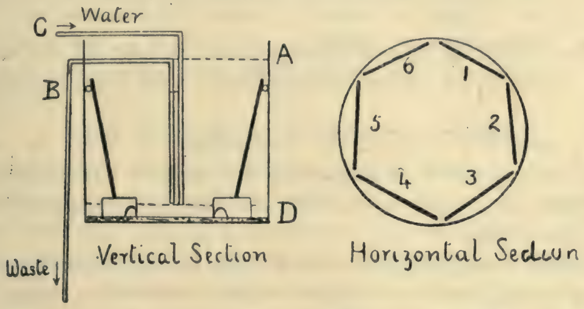

Plate No.	Initial weight, grams.	Loss in weight, grams.	Mean loss, grams.	Relative corrosion.
1	75·53	0·33	0·31	100
2	71·89	0·28		
3	72·82	0·47	0·48	155
4	72·46	0·49		
5	72·98	0·44	0·45	145
6	60·90	0·46		

A second similar set of experiments entirely confirmed these results.

It is evident that the plates which had been placed in acid corroded more rapidly than the others, showing that the acid is not immediately washed out of the iron by water. That plates 5 and 6 corroded more rapidly than 1 and 2 shows that either the alkali had not had time to soak in as far as the acid had done, or, what is more probable, that it had neutralised the acid in the pores of the metal and had remained there as sodium sulphate, not being completely washed out in the final rinsings, and thus stimulating the corrosion, although not to so great an extent as the free acid would have done. All these experiments therefore agree in illustrating the porous nature of iron, and an explanation is thus afforded for the fact, well known to painters, that the acid is excessively difficult to remove, by the mere process of washing, from the surface iron that has been treated with acid to remove the adherent mill scale. This, in fact, is one of the great difficulties in the trade.

Conclusions.

The above experiments lead us to the following important conclusions:

(1) The surface of iron is slightly porous, so that when the metal is immersed in certain solutions the latter are absorbed to a minute extent.

This observation is of particular interest in view of the numerous catalytic reactions in which finely divided iron plays an important part.

(2) The passivity induced by immersion of iron in alkaline solutions, such as those of potassium and sodium hydroxides, is due to absorption of minute quantities of these substances within the pores of the metal.

This affords a ready explanation for the facts that such passivity:

(*a*) Is gradually lost by the iron when immersed in water, for the alkali slowly diffuses out again.

(*b*) May be rapidly removed by the addition of small quantities of any acid.

(*c*) May be retained for long periods, if kept dry, since the alkali is unable to escape.

(*d*) Varies in intensity according to the concentration of the alkali and the time during which the metal is "soaked."

(3) There are more kinds of passivity than one.

Since the above explanation of the passivity induced by alkaline solutions cannot possibly apply to that caused by powerful oxidisers such as nitric acid, we have here for the first time a definite proof that there are more kinds of passivity than one. This removes one of the great difficulties in the way of accepting any theory of passivity, for it is generally assumed that one theory should explain every case. De Benneville (*J. Iron Steel Inst.*, 1897, ii, 40) showed that the passivity induced by concentrated silver nitrate solution is identical in kind with that resulting from immersion in strong nitric acid; and this is what we might expect when two such similar solutions are employed. Fredenhagen (*Zeitsch. physikal. Chem.*, 1908, **63**, 1), on the other hand, has observed differences in the behaviour of iron rendered passive by anodic polarisation in sulphuric acid from that passivified by immersion in strong nitric acid. He therefore suggests that the two kinds of passivity may be different, but no definite proof has been forthcoming. Similarly Senderens (*J. Iron Steel Inst.*, 1897, ii, 78) draws attention to the fact that unannealed iron is more active than annealed iron when both are immersed in nitric acid, whereas the reverse is true in silver nitrate solution. Whilst these peculiarities may simply be due to differences in intensity of the passivity, in view of the above proof that different kinds of passivity can exist, it is clear that each case must be judged on its own merits, and no one theory required to explain every case.

Furthermore, in studying the phenomena of passivity, particular care must be taken to ensure the absence of traces of solutions within the pores of the metal. Herein probably is to be found an explanation for many of the conflicting statements as to the properties of passive iron, with which the literature of passivity abounds.

The Relation of Passivity to Corrosion.

These results have a very important bearing on the various theories advanced to account for corrosion. In a recent paper (Proc., 1910, **26**, 179) an apparatus is described showing that water may be distilled on to iron in an acid-free atmosphere without producing any trace of rust, and this experiment may be regarded as a definite proof of the acid theory of corrosion. Dunstan and Hill (*loc. cit.*, p. 1848), however, argue that the absence of corrosion is attributable to passivity induced by previous immersion of the metal in potassium hydroxide, and that, until this passivity has been removed by traces of acid, the iron cannot rust.

In order to show that continued washing with water would remove the alkali from the pores of the metal and render it active, strips of iron which had been rendered passive as above by prolonged immersion in concentrated potassium hydroxide solution were plunged into boiling water and the latter allowed to boil vigorously for varying lengths of time. The strips were then removed, and tested for passivity in the usual way. It was found that boiling for three minutes produced but little effect, the metal remaining decidedly passive; after ten minutes' boiling the metal was only slightly passive, and soon corroded; but after boiling for half an hour the passivity had entirely disappeared. In my experiments, therefore, in which the iron, in the apparatus referred to above, was washed by condensing steam on it for many hours, there cannot be the slightest doubt that all the alkali was completely washed out of the pores. Hence the fact that an acid must be introduced into the apparatus, which Dunstan himself acknowledges, in order to induce corrosion, is simply a re-statement of the acid theory of corrosion. The main function of the alkali is to dissolve out the traces of acid from the pores of the metal, and thus to render its surface clean and free from acid.

The Action of Various Electrolytic Solutions on Iron.

Dunstan and Hill (*loc. cit.*, p. 1850) give a table purporting to illustrate the action of various electrolytic solutions on iron, zinc, aluminium, copper, and magnesium. Heyn and Bauer, however, in their monumental researches (*Mitt. Königl. Material-prüfungsamt*, 1908, **26**, 2) into the action of various solutions on iron clearly demonstrated in a quantitative manner for all the common salts the important effect produced by varying the concentration of the electrolyte; thus, not only does dilute sodium carbonate fail to inhibit the corrosion of iron, but it actually stimulates it, whereas in the presence of more concentrated solutions iron may be kept bright for an indefinite time. The same is true for the ferro- and ferri-cyanides of potassium. Furthermore, J. H. Brown and the author (Trans., 1911, **99**, 1302) have shown that the temperature at which the experiments are carried out is likewise an important item; thus, whilst dilute sodium chloride solutions above 13° tend to retard corrosion, below this temperature they stimulate it.

In the table drawn up by Dunstan and Hill both the temperature and concentration are omitted, so that the results are not merely useless but positively misleading. It is interesting to note at the bottom of the table that potassium ferrocyanide is said both to inhibit and to allow the corrosion of iron. This is true for concentrations of 2·0 grams and 0·2 gram per litre respectively. If the second potassium ferrocyanide is a misprint for the ferricyanide, the statement is less true. One per cent. solutions of either salt will completely inhibit corrosion.

This shows how important it is that full quantitative particulars should be given, for qualitative mixtures chosen at random inevitably lead to confusion.

In conclusion, I have pleasure in acknowledging my indebtedness to the Research Fund Committee for a grant which is enabling me to continue these studies of corrosion.

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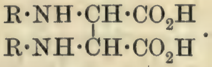
VI.—*The Action of Aliphatic Amines on* s-*Dibromosuccinic Acid. Part I.*

By EDWARD PERCY FRANKLAND and HENRY EDGAR SMITH

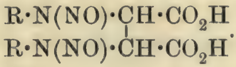
THE authors have investigated the action of *n*-propylamine and *n*-butylamine on *s*-dibromosuccinic acid in alcoholic solution with the view of obtaining the dialkylaminosuccinic acids of the type



$$\begin{array}{l} R\cdot NH\cdot CH\cdot CO_2H \\ R\cdot NH\cdot CH\cdot CO_2H \end{array}.$$

These compounds were prepared by the method described by E. P. Frankland (Trans., 1911, **99**, 1775) for dibenzylaminosuccinic acid, and the reaction appeared to proceed in a similar manner, yielding in the case of propylamine the amine salts of dibromosuccinic acid and bromomaleic acid, but no bromopropylaminosuccinic acid. The final product was in each case a mixture of the dialkylaminosuccinic acid and its amine salt, the pure amino-acid being obtained by recrystallisation from hydrochloric acid or ammonia.

The dipropylamino- and dibutylamino-succinic acids are crystalline solids, sparingly soluble in water, and forming salts with copper and with hydrochloric acid, and dinitroso-derivatives of the type



$$\begin{array}{l} R\cdot N(NO)\cdot CH\cdot CO_2H \\ R\cdot N(NO)\cdot CH\cdot CO_2H \end{array}.$$

EXPERIMENTAL.

Action of Propylamine on s-*Dibromosuccinic Acid in Ethyl-alcoholic Solution.*

(*a*) *Dipropylamine Salt of Dibromosuccinic Acid and Monopropylamine Salt of Monobromomaleic Acid.*—A solution of 10·0 grams of dibromosuccinic acid in 100 c.c. of absolute ethyl alcohol was treated with 8·55 grams of propylamine (4 molecules). The solution became warm, and a white precipitate was deposited. This was collected, washed with alcohol and ether, and dried; it weighed 14·3 grams. Theory requires 14·28 grams of the dipropylamine salt of dibromosuccinic acid. The substance crystallised in small, hexagonal plates, and melted at 139°,[*] decomposing at 165°:

0·1714 gave 97·03 c.c. CO_2 and 9·57 c.c. N_2.[†] $C=30·48$; $N=7·01$.

$C_{10}H_{22}O_4N_2Br_2$ requires $C=30·46$; $N=7·11$ per cent.

A small portion of the substance was dissolved in water, and an aqueous solution of silver nitrate added. A white, crystalline precipitate of the *disilver* salt of *dibromosuccinic acid* was deposited, which darkened on exposure to light. On warming this substance in aqueous solution, silver bromide separated:

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[*] All temperatures here given are uncorrected.

[†] Dry CO_2 and N_2 at N.T.P.; carbon and nitrogen combustion in a vacuum.

0·1586 gave 0·1205 AgBr. Ag=43·65.

$C_4H_2O_4Br_2Ag_2$ requires Ag=44·08 per cent.

A portion of the dipropylamine salt was dissolved in alcohol containing a little water, and the solution evaporated to dryness on the water-bath. The residue was then dissolved in absolute alcohol. Propylamine hydrobromide (Found, Br=56·71. Calc., Br=57·14 per cent.) and the monopropylamine salt of monobromomaleic acid were isolated from the solution by fractional crystallisation from alcohol. The *monopropylamine* salt of *monobromomaleic acid* separated from alcoholic solution in long, needle-shaped crystals, which melted at 93°.

The cold aqueous solution decolorised permanganate:

0·1586 gave 97·96 c.c. CO_2 and 6·81 c.c. N_2. C=33·25; N=5·39.

$C_7H_{12}O_4NBr$ requires C=33·07; N=5·51 per cent.

(*b*) *Dipropylaminosuccinic Acid.*—A solution of 10·0 grams of dibromosuccinic acid in 100 c.c. absolute alcohol was treated with 8·55 grams of propylamine, and heated to boiling on the water-bath. The dipropylamine salt dissolved, and after heating for about forty-five minutes another substance began to deposit, complete precipitation being obtained after about seven hours' heating.

The substance was washed with alcohol and ether, and when dried weighed 5·9 grams. It decomposed at 283°. A little more of this substance was obtained by evaporating the mother liquor.

This substance, dipropylaminosuccinic acid, was purified by dissolving it in the least possible quantity of concentrated hydrochloric acid, and diluting with water, when a white powder was immediately deposited. The mother liquor yielded some propylamine hydrochloride, and when benzoylated, *n*-propylbenzamide was obtained, melting at 85°. (Found, C=73·11; H=8·18; N=8·78. Calc., C=73·62; H=8·00; N=8·59 per cent.)

Dipropylaminosuccinic acid crystallised from aqueous solution in plates. It was insoluble in alcohol or ether, sparingly soluble in hot water, and readily so in concentrated acids and ammonia. A specimen of dipropylaminosuccinic acid recrystallised from ammonia decomposed at 278°. The aqueous solution was neutral to litmus:

0·1004 gave 96·25 c.c. CO_2 and 9·65 c.c. N_2. C=51·62; N=12·07.
0·0858 ,, 0·1618 CO_2 and 0·0676 H_2O. C=51·43; H=8·75.

$C_{10}H_{20}O_4N_2$ requires C=51·72; H=8·62; N=12·07 per cent.

Monohydrochloride of Dipropylaminosuccinic Acid.

On warming a solution of dipropylaminosuccinic acid in 25 per cent. hydrochloric acid on the water-bath, the unchanged acid could not be reprecipitated by dilution of the solution with water. After evaporating the solution to a small bulk and stirring with alcohol, a white, crystalline solid was deposited.

On recrystallising from a solution in alcohol containing a few drops of hydrochloric acid, a hydrochloride separated in long, needle-shaped crystals, which melted and decomposed at 187°. It was readily soluble in water, and insoluble in absolute alcohol or ether. The aqueous solution was acid to litmus:

0·1187 gave 97·53 c.c. CO_2 and 9·77 c.c. N_2. C=44·24; N=10·34.
0·8139 „ 0·4262 AgCl. Cl=12·96.
$C_{10}H_{20}O_4N_2,HCl$ requires C=44·69; N=10·43; Cl=13·22 per cent.

Dihydrochloride of Dipropylaminosuccinic Acid.

When dipropylaminosuccinic acid was dissolved in a small volume of concentrated hydrochloric acid and the solution evaporated over soda-lime and sulphuric acid in a vacuum, a white solid was deposited. This was stirred with concentrated hydrochloric acid, collected, and washed with dry acetone and ether. It decomposed somewhat on further treatment with acetone and ether, giving a pink solid, which had a chlorine content lying between those of the mono- and di-hydrochlorides of dipropylaminosuccinic acid. The first product gave the following result on analysis:

0·7560 gave 0·7874 AgCl. Cl=25·77.
$C_{10}H_{20}O_4N_2,2HCl$ requires Cl=23·28 per cent.

On concentrating a solution of the substance in aqueous ammonia on the water-bath, dipropylaminosuccinic acid was deposited. It decomposed at 278°.

Dinitrosodipropylaminosuccinic Acid.

One gram of dipropylaminosuccinic acid was dissolved in a small volume of concentrated hydrochloric acid, and the solution diluted slightly with water. On adding a solution of the molecular quantity of sodium nitrite (2 molecules) to the well-cooled acid solution with frequent stirring, a white solid was gradually deposited in groups of minute needles. This was collected, washed with water, and dried. The substance was insoluble in cold water, extremely soluble in alcohol or ether. It melted and decomposed at 157°, and gave the Liebermann test for a nitroso-compound:

0·1051 gave 80·24 c.c. CO_2 and 16·2 c.c. N_2. C=41·10; N=19·36.
$C_{10}H_{18}O_6N_4$ requires C=41·38; N=19·31 per cent.

Copper Salt of Dipropylaminosuccinic Acid.

An excess of copper carbonate was gradually added to 1 gram of dipropylaminosuccinic acid in boiling water. The solution was made up to 200 c.c. with water, boiled for some time, and filtered while hot.

The residue was then boiled with dilute acetic acid to remove the excess of copper carbonate, thoroughly extracted with boiling water, filtered, washed with alcohol and ether, and dried. The copper salt was a light blue powder, insoluble in water and organic solvents.

Under the influence of heat it gradually changed colour to a light red at about 230°; it then gradually assumed the colour of reduced copper at 240—245°, shot up the melting-point tube at 250°, and finally decomposed at 262—263°:

0·4756 gave 0·1309 Cu_2S. Cu=21·97.
$C_{10}H_{18}O_4N_2Cu$ requires Cu=21·66 per cent.

Action of n-*Butylamine on* s-*Dibromosuccinic Acid.*

A solution of 5·0 grams of dibromosuccinic acid in 70 c.c. absolute alcohol was treated with 5·4 grams (4 molecules) of *n*-butylamine. The solution became warm, and deposited the *di*-n-*butylamine* salt of dibromosuccinic acid as a white, crystalline precipitate. On heating on the water-bath, this precipitate quickly dissolved, and after forty-five minutes' heating another precipitate began to deposit. This was collected from time to time, washed with alcohol and ether, and dried. It weighed 3·05 grams, and decomposed at 288°. After purification by dissolving in the least possible quantity of concentrated hydrochloric acid and precipitating with water, the substance decomposed at 289—290°. It was sparingly soluble in hot water, insoluble in alcohol and in ether, and easily soluble in concentrated acids and aqueous ammonia. The aqueous solution was neutral to litmus:

0·1422 gave 0·2872 CO_2 and 0·1206 H_2O. C=55·08; H=9·40.
0·0932 ,, 95·61 c.c. CO_2 and 8·11 c.c. N_2. C=55·23; N=10·93.
$C_{12}H_{24}O_4N_2$ requires C=55·38; H=9·23; N=10·77 per cent.

Monohydrochloride of Dibutylaminosuccinic Acid.

A solution of dibutylaminosuccinic acid in concentrated hydrochloric acid was evaporated to small bulk on the water-bath, and the residue dissolved in warm alcohol, from which a white, crystalline solid separated out. This was recrystallised from alcohol containing a few drops of concentrated hydrochloric acid, and was deposited in shining plates, which decomposed at 195—196°. It was readily soluble in water, sparingly so in alcohol, and insoluble in ether. The aqueous solution was strongly acid to litmus:

0·0996 gave 0·0468 AgCl. Cl = 11·62.

$C_{12}H_{24}O_4N_2,HCl$ requires Cl = 11·97 per cent.

Dinitrosodibutylaminosuccinic Acid.

0·9 Gram of dibutylaminosuccinic acid was dissolved in a small volume of concentrated hydrochloric acid, and the solution diluted somewhat with water. On adding a solution of the molecular quantity (2 molecules) of sodium nitrite, a precipitate was deposited in minute needles. The mixture was allowed to remain for a time, and the precipitate collected. After washing with water and drying, the substance melted and decomposed at 147°. It was insoluble in cold water, and extremely soluble in alcohol or ether:

0·1034 gave 86·41 c.c. CO_2 and 14·31 c.c. N_2. C = 44·99; N = 17·39.

$C_{12}H_{22}O_6N_4$ requires C = 45·28; N = 17·61 per cent.

*Copper Salt of Di-*n*-butylaminosuccinic Acid.*

This compound was prepared as described for the copper salt of dipropylaminosuccinic acid. It was a light blue powder, insoluble in water and organic solvents. It exhibited characteristic behaviour when heated. It changed to light red at 230—235°, shot up the tube at 245—250°, and finally decomposed at 265—267°:

0·3816 gave 0·0943 CuO. Cu = 19·73.

$C_{12}H_{22}O_4N_2Cu$ requires Cu = 19·75 per cent.

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VII.—*Complex Thio-oxalates.*

By CHARLES STANLEY ROBINSON and HUMPHREY OWEN JONES.

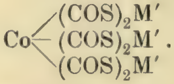
IN a former paper (Jones and Tasker, Trans., 1909, **95**, 1904) it was shown that highly coloured complex compounds are formed when solutions of nickel or cobalt salts are added to a solution of potassium dithio-oxalate. These colours persist through a long range of dilution, being appreciable at a dilution of one part of nickel or cobalt in 40,000,000 of water. A complex salt containing nickel was isolated and shown to have the composition of a potassium salt of nickelodithio-oxalic acid, $H_2(COS)_4Ni$. The intense colour of solutions of this salt is so remarkable that it was considered of interest to prepare other salts, and also to isolate the compound formed by the interaction of solutions of a cobalt salt and of potassium dithio-oxalate.

We have prepared several metallic and some organic salts of nickelodithio-oxalic acid; a similar series of salts of palladiodithio-oxalic acid has been obtained, and it has also been shown that salts of the complex ferrodithio-oxalic acid are formed, but these are extremely unstable.

The complex salts derived from cobaltidithio-oxalic and rhodiidithio-oxalic acids have been isolated.

The molecular weights and electrical conductivities in aqueous solution of some of these salts have been determined. The results of these experiments indicate that nickelodithio-oxalic acid and cobaltidithio-oxalic acids are dibasic and tribasic respectively. The thermal decomposition of certain salts of these acids was studied with a view to obtain some insight into their constitutions. The experimental evidence at present available is in agreement with the formula $M'(COS)_2{\cdot}Ni{\cdot}(COS)_2M'$ for salts of nickelodithio-oxalic acid, which is shown to be an acid of about the same strength as sulphuric acid. The salts of palladio- and ferro-dithio-oxalic acids are derived from dibasic acids of similar constitution.

The cobalti- and rhodii-dithio-oxalates are, however, derived from tribasic acids, and the formula of the cobalt compound can best be represented as:



$$Co\begin{cases}(COS)_2M'\\(COS)_2M'\\(COS)_2M'\end{cases}.$$

When potassium cyanide is added to solutions of potassium nickelodithio-oxalate, potassium palladiodithio-oxalate, or potassium ferrodithio-oxalate, the colour of these solutions is discharged.

It was found that approximately four molecules of potassium cyanide were needed to decolorise one molecule of potassium nickelodithio-oxalate.

Potassium cyanide, however, decomposes cobalti- or rhodii-dithio-oxalates only when concentrated.

Experiments are in progress with the object of preparing the free acids and the esters of the above-mentioned complex acids, and also for preparing similar complex salts derived from thiomalonates, thiosuccinates, and thiocarbonates, with the view of tracing a relationship between the constitution, colour, and stability of these complex compounds.

As large quantities of potassium dithio-oxalate were needed for this investigation, experiments were made with the object of determining the best conditions for the preparation of this salt. As ethyl and phenyl mercaptans are objectionable on account of their odours, amyl dithio-oxalate was prepared by the action of amyl mercaptan on oxalyl chloride. It is a pale yellow oil, boiling at 205°/20 mm. From this ester the potassium salt is produced by saponification with alcoholic potassium hydrosulphide, the best yield being obtained when the calculated quantities of a normal solution of potassium hydrosulphide and amyl ester are gently warmed together for a short time.

Sodium dithio-oxalate, $(COSNa)_2$, which had not been previously obtained, was prepared by the action of alcoholic sodium hydrosulphide on amyl dithio-oxalate.

When amyl dithio-oxalate is warmed with a slight excess of *N*-alcoholic sodium hydrosulphide solution, saponification takes place, and the sodium salt separates on keeping. It was recrystallised from hot alcohol, and separated as colourless plates. A solution of this salt gives the same characteristic colour as the potassium salt when mixed with a solution of a nickel salt:

0·1570 gave 0·1340 Na_2SO_4. Na = 26·60.

$(COSNa)_2$ requires Na = 26·72 per cent.

With the view of obtaining barium dithio-oxalate, cold concentrated solutions of barium chloride and potassium dithio-oxalate were mixed. A white precipitate separated, but, contrary to expectation, this precipitate was found to be a mixture of barium sulphide and barium oxalate.

Aniline dithio-oxalate, $(COS\cdot NH_3\cdot C_6H_5)_2$, separates in orange-coloured plates when cold aqueous solutions of aniline hydrochloride and potassium dithio-oxalate are mixed. Its solutions in warm water, cold alcohol, or acetone undergo rapid decomposition with evolution of hydrogen sulphide and separation of oxanilide.

Owing to the extreme ease with which this salt decomposes, it could not be prepared pure. Freshly prepared aqueous solutions of salt give the characteristic nickelodithio-oxalate colour on admixture with a solution of a nickel salt, but no colour is developed if the solution of the aniline salt is allowed to remain for some time before adding the nickel salt.

Potassium nickelodithio-oxalate, $K_2(COS)_4Ni$, separates as a black, crystalline precipitate when equal weights of nickel chloride and potassium dithio-oxalate in concentrated aqueous solutions are mixed. This salt crystallises from hot water in dark red octahedra.

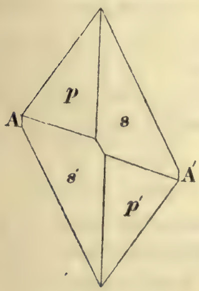
As the composition of this salt is of fundamental importance, it was analysed several times.

The results obtained for carbon, hydrogen, and sulphur agree so closely with those given in the former paper (*loc. cit.*, p. 1908) that the determination of the percentage of nickel only need be given here to supplement the results already published:

0·4200 gave 0·0870 NiO. Ni = 16·2.

$K_2(COS)_4Ni$ requires Ni = 15·8 per cent.

Sometimes it was found that potassium nickelodithio-oxalate separated as needles, whilst at other times it separated as octahedra from aqueous solutions. Both forms had the same composition, and on investigation this was found to be a case of dimorphism. On cooling a solution of potassium nickelodithio-oxalate to 22°, octahedra only separate, but if the solution is cooled rapidly to 10°, needles separate. Above 20°, needles in contact with water change slowly into octahedra, whilst if the octahedra are kept under water in an ice chamber for several hours, they change slowly into needles.



The transition temperature is approximately 20°.

Mr. A. Hutchinson has kindly provided the following report on the octahedral form based on measurements made by Mr. A. F. Hallimond.

"Crystal system: Oblique. $a:b:c = 1·7637:1:2·8664$. $\beta = 70°56'$.

Forms observed: $p\{111\}$ and $s\{\bar{1}11\}$ large, $A\{100\}$ small. The small black crystals are about 3 mm. in length, and belong to the holohedral sub-class of the oblique system. The habit is pyramidal, *p* and *s* being equally developed. This is shown in the figure, which is a plan on the plane of symmetry.

The following angles were observed:

Angle measured.	No. of measurements.	Limits	Mean observed.	Calculated.
ps $=(111):(\bar{1}11)$	16	58°26′—58°52′	58°35′	*
ps′ $=(111):(11\bar{1})$	14	34 30 —34 50	34 44	*
ss′ $=(\bar{1}11):(11\bar{1})$	7	61 16 —61 23	61 19½	*
pp′ $=(111):(\bar{1}1\bar{1})$	8	76 30 —77 42	77 11½	77°21′
Ap $=(100):(111)$	4	55 36 —56 5	55 52	55 46½
As′ $=(100):(11\bar{1})$	4	65 33 —65 40	65 36½	65 38½

Cleavage: *A*{100} perfect, *B*{010} imperfect.

The specific gravity is 2·132 at 18·4° (compared with water at 4°). In very thin flakes the crystals are transparent and transmit brownish-red light. The extinction of a cleavage flake parallel to *A* was found to be parallel to *B*, and a flake parallel to *B* appeared to extinguish parallel to the edge *AB*. The crystals are very strongly pleochroic, vibrations parallel to the edge *AB* being totally absorbed. If the light is vibrating perpendicular to *A*{100}, only deep red is transmitted; pale brown is transmitted if the vibrations are perpendicular to *B*. An approximate value of 1·54 was obtained by the immersion method for the index of refraction of light vibrating perpendicular to *A*."

The potassium salt is too sparingly soluble in cold water to allow of trustworthy determinations of its molecular weight in solution to be made. The electrical conductivity, however, shows that it ionises into three ions.

Electrical Conductivity of Potassium Nickelodithio-oxalate in Aqueous Solution.

Concentration ………………	*M*/32	*M*/64	*M*/1024	*M*/2048
Molecular conductivity ……	217·3	227·4	265·1	276·0

If E_{32} and E_{1024} be the equivalent conductivities at dilutions $M/32$ and $M/1024$ per litre, then

$$\frac{E_{1024}-E_{32}}{10} = \frac{265{\cdot}1/2 - 217{\cdot}3/2}{10} = 2{\cdot}39.$$

The salt is therefore derived from a dibasic acid, for which

$$\frac{E_{1024}-E_{32}}{10} = 2.$$

With increasing dilution a constant value for the conductivity cannot be obtained.

Barium nickelodithio-oxalate, $Ba(COS)_4Ni,4H_2O$, is sparingly soluble in cold water, and is precipitated on mixing solutions of barium chloride and potassium nickelodithio-oxalate. It separates on cooling hot aqueous solutions in black, iridescent needles:

0·7780 gave 0·3485 $BaSO_4$. Ba = 26·33.
Total $BaSO_4$ = 1·395. S = 24·8.
0·4225 gave 0·0640 NiO. Ni = 11·9.
0·5060, dried in a desiccator for two days, gave 0·1680 CO_2 and 0·0760 H_2O. C = 9·05; H_2O = 15·0.

(This result indicates that the salt still retained some water.)

$Ba(COS)_4Ni,4H_2O$ requires Ba = 26·9; S = 25·2; Ni = 11·6; C = 9·44; H_2O = 14·10 per cent.

Lead Nickelodithio-oxalate, $Pb(COS)_4Ni,2H_2O$. — This salt separates in lustrous needles when solutions of lead acetate and potassium nickelodithio-oxalate are mixed. It is almost insoluble in cold water, and decomposes on boiling with separation of lead sulphide:

0·6092 gave 0·1935 CO_2 and 0·0435 H_2O. C = 8·63; H_2O = 7·1.
0·5220 „ 0·2860 $PbSO_4$ and 0·6780 $BaSO_4$. Pb = 37·4; S = 23·3.

$Pb(COS)_4Ni,2H_2O$ requires C = 8·8; H_2O = 6·6; Pb = 38·2; S = 23·6 per cent.

Ammonium nickelodithio-oxalate, $(NH_4)_2(COS)_4Ni,4H_2O$, was prepared by mixing hot concentrated solutions containing equivalent quantities of ammonium sulphate and barium nickelodithio-oxalate. After filtering off the barium sulphate, the remaining solution on evaporation yields the ammonium nickelodithio-oxalate in beautiful, lustrous, almost black needles.

On boiling with potassium hydroxide solution, 1·15 gave off ammonia which neutralised 5·57 c.c. of *N*-sulphuric acid. NH_4 = 8·71.

0·5955 gave 0·2505 CO_2 and 0·202 H_2O. C = 11·5; H = 3·77.

The residue from the combustion was reduced, ignited, and gave 0·1090 NiO. Ni = 14·4.

$(NH_4)_2(COS)_4Ni,4H_2O$ requires NH_4 = 8·84; C = 11·79; H = 3·9; Ni = 14·5 per cent.

Molecular Weight of Ammonium Nickelodithio-oxalate.

0·192, in 25 c.c. of water, gave $\Delta t - 0·1°$. M.W. = 138·2, but $(NH_4)_2(COS)_4Ni,4H_2O$ requires 407.

Hence it appears that the salt has dissociated into three ions.

Conductivity of Ammonium Nickelodithio-oxalate in Aqueous Solution.

Concentration	$M/32$	$M/1024$
Molecular conductivity......	227	276

$$\frac{E_{1024}-E_{32}}{10} = \frac{276/2-227/2}{10} = 2\cdot4.$$

The salt is therefore derived from a dibasic acid.

At greater dilutions the conductivity increases still more, and within the limits of practical determination a constant value cannot be reached.

Sodium nickelodithio-oxalate, $Na_2(COS)_4Ni,2\frac{1}{2}H_2O$, was prepared by mixing concentrated solutions of sodium dithio-oxalate and nickel chloride. The sparingly soluble sodium nickelodithio-oxalate separates in black prisms, which do not exhibit such a high lustre as the other salts:

0·2750 gave 0·1255 CO_2 and 0·0310 H_2O. $C=12\cdot44$; $H_2O=11\cdot3$.
$Na_2(COS)_4Ni,2\frac{1}{2}H_2O$ requires $C=12\cdot3$; $H_2O=11\cdot5$ per cent.

When mercuric chloride in excess is added to a solution of potassium nickelodithio-oxalate, the mercury salt is not obtained, but the solution is decolorised, and a yellow precipitate is formed, which was found to be a mixture of mercury sulphide with mercury oxalate.

When excess of mercuric chloride is avoided, a coloured precipitate, probably of mercury nickelodithio-oxalate, is formed, and gradually decomposes, giving the yellow solid and carbon monoxide.

The nickel, cobalt, and silver salts of nickelodithio-oxalic acid decompose on keeping, with formation of a sulphide of the heavy metal. In fact, with the exception of lead, few salts of a metal which yields an insoluble sulphide are sufficiently stable to be prepared in the ordinary way.

Aniline nickelodithio-oxalate, $(C_6H_5\cdot NH_3)_2(COS)_4Ni$, separates as a reddish-brown, microcrystalline powder when a solution of aniline hydrochloride is added to one of potassium nickelodithio-oxalate:

0·3200 gave 0·4576 CO_2, 0·0930 H_2O, and 0·0505 NiO. $C=39\cdot0$; $H=3\cdot24$; $Ni=12\cdot4$.
0·2950 gave 0·5590 $BaSO_4$. $S=26\cdot0$.
0·2500 „ 11·4 c.c. N_2 at 0° and 760 mm. $N=5\cdot72$.
$(C_6H_5\cdot NH_3)_2(COS)_4Ni$ requires $C=39\cdot4$; $H=3\cdot3$; $Ni=12\cdot1$; $S=26\cdot28$; $N=5\cdot75$ per cent.

This salt is so insoluble in water containing an excess of aniline hydrochloride that the supernatant liquid is colourless; it was thought therefore that its formation might be utilised in the estimation of aniline. Fairly accurate results were obtained with concentrated solutions, but at greater dilutions the method was not a success, probably owing to hydrolysis of the salt.

Thermal Decomposition of Aniline Nickelodithio-oxalate.

When aniline nickelodithio-oxalate is heated, decomposition begins at 180°, and is completed slowly at 210°. Among the products of this decomposition, oxanilide, aniline, hydrogen sulphide, and carbon monoxide were identified, whilst the residue contained only nickel and sulphur.

An attempt was made to estimate these decomposition products with the object of ascertaining the mode of decomposition, and, if possible, of obtaining some insight into the constitution of the salt. A weighed quantity of the salt was heated to 210° in a hard glass tube fitted to an air condenser.

The carbon monoxide and hydrogen sulphide escaped, and the contents of the tube and condenser were extracted with hot benzene, which dissolved both the aniline and the oxanilide. This benzene solution was shaken with a solution of hydrochloric acid. The aqueous layer containing aniline hydrochloride was separated from the benzene layer containing the oxanilide. Both solutions were evaporated to dryness, and the residues weighed.

It was only possible to get approximate values for the amounts of aniline and oxanilide, partly on account of the loss of aniline due to hydrolysis, and partly on account of the slight solubility of oxanilide in benzene.

Experiment I.—0·813 gave 0·241 aniline hydrochloride and 0·134 oxanilide. Hence aniline per gram-molecule = 103 grams; oxanilide = 80 grams.

Experiment II.—0·860 gave 0·250 aniline hydrochloride and 0·160 oxanilide. Hence aniline per gram-molecule = 99 grams; oxanilide = 89 grams.

Experiment III.—1·34 gave 0·334 aniline hydrochloride and 0·278 oxanilide. Hence aniline per gram-molecule = 93 grams; oxanilide = 109 grams.

The gases evolved when a weighed quantity of the salt was heated in a vacuum were collected by means of a Töpler pump, and the volume of gas was measured before and after treatment with concentrated aqueous potassium hydroxide solution.

The residual gas was carbon monoxide, whilst the gas absorbed by the alkali was hydrogen sulphide, with possibly carbonyl sulphide.

Experiment I.—0·198 gave 44·5 c.c. at 18° and 756 mm., of which 18·7 c.c. were carbon monoxide.

Total gas = 108·5 litres per gram-molecule of salt.
Carbon monoxide = 44·3 " " "
Residue = 0·043 = 110·5 grams " "

Experiment II.—

Total gas = 106·2 litres per gram-moleculo of salt.
Carbon monoxide = 43·0 " " "
Residue = 106·0 grams " "

Experiment III.—

Total gas = 110·0 litres per gram-molecule of salt.
Carbon monoxide = 43·5 " " "
Residue = 106·0 grams " "

From these results, which are fairly consistent with each other, it appears that each molecule of aniline nickelodithio-oxalate gives two molecules of carbon monoxide and five molecules of hydrogen sulphide or of a mixture of this gas with carbonyl sulphide. It was found impossible to decide whether both these gases were present by liquefaction and fractional distillation, but the behaviour of the gas towards an aqueous solution of lead acetate indicated that some carbonyl sulphide was present.

In order to ascertain if carbonyl sulphide was present, and to determine its amount, *phenyltrimethylammonium nickelodithio-oxalate*, $[C_6H_5\cdot N(CH_3)_3]_2(COS)_4Ni$, was prepared by mixing solutions of the iodide of the organic base with the potassium salt of the acid, when it separated in diamond-shaped, red plates, showing a remarkably high lustre, which melted and decomposed at 215—216°:

0·2030 gave 0·3430 CO_2 and 0·0884 H_2O. C = 46·1; H = 4·84.
$[C_6H_5\cdot N(CH_3)_3]_2(COS)_4Ni$ requires C = 46·2; H = 4·91 per cent.

A weighed quantity of this salt was heated to about 250° in a stream of dry nitrogen, the evolved gases were passed through a U-tube cooled by ice, in order to condense dimethyl sulphide, and then into a receiver cooled in liquid air.

In this way the carbonyl sulphide was solidified, whilst the nitrogen and most of the carbon monoxide escaped; a small amount of carbon monoxide, however, appears to be retained by the solid oxysulphide. The cooled receiver was then connected to a gas burette, and by allowing the temperature to rise slowly the solidified gas vaporised, and was swept into the burette by a stream of nitrogen.

The volume of gas was measured before and after treatment with aqueous potassium hydroxide; the contraction represents the volume of carbonyl sulphide evolved from the phenyltrimethylammonium salt. From this the number of litres of carbonyl sulphide evolved from a gram-molecule of phenyltrimethylammonium nickelodithio-oxalate is calculated.

It seems reasonable to assume that the gram-molecule of the aniline salt gives the same amount of carbonyl sulphide.

Experiment I.—0·412 gave 16·3 c.c. COS, corrected to 0° and 760 mm. Hence one gram-molecule of the salt gives 22·6 litres COS.

Experiment II.—0·405 gave 15·6 c.c. COS, corrected to 0° and 760 mm. Hence one gram-molecule of the salt gives 22·0 litres COS.

Therefore one gram-molecule of the salt yields one gram-molecule of carbonyl sulphide.

The results obtained in the above experiments indicate that the decomposition of aniline nickelodithio-oxalate is best represented by the equation:

$$2Ni(COS)_4(C_6H_5{\cdot}NH_3)_2 = Ni_2S_3 + 4CO + 2COS + 3H_2S + 2C_6H_5{\cdot}NH_2 + (CO{\cdot}NH{\cdot}C_6H_5)_2.$$

Products of Decomposition per Gram-molecule of Salt.

	Found.	Calculated.
Carbon monoxide	43·8 litres	44·4 litres
Carbonyl sulphide	22·3 ,,	22·2 ,,
Hydrogen sulphide............	42·0 ,,	33·3 ,,
Aniline...........................	97·0 grams	93·0 grams
Oxanilide........................	109·0 ,,	120·0 ,,
Nickel sulphide	110·5 ,,	103·0 ,,

The only discrepancy is observed in the amount of hydrogen sulphide found, and as this value is obtained by differences, this may be due to the decomposition of some of the carbonyl sulphide into hydrogen sulphide and carbon dioxide by moisture.

A very large number of organic bases, such as aromatic amines, quinoline derivatives, and alkaloids, give crystalline nickelodithio-oxalates which are very sparingly soluble in water. Of these, the *guanidine* salt is the most striking, as it is very sparingly soluble in cold water, and separates from hot water in long, black, lustrous needles.

Nickelodithio-oxalic Acid.

It seemed reasonable to suppose that by mixing sulphuric acid and barium nickelodithio-oxalate in equivalent quantities, free nickelodithio-oxalic acid would be obtained in solution.

However, on evaporation of the resulting solution, after removal of the barium sulphate, decomposition with evolution of hydrogen sulphide and separation of nickel oxalate took place.

The behaviour of this acid in solution can, however, be followed by measuring the electrical conductivity.

A solution of barium nickelodithio-oxalic was made, and its electrical conductivity measured; 10 c.c. of this solution were mixed with 10 c.c. of an equivalent sulphuric acid solution. The resulting solution, neglecting the barium sulphate which is precipitated, should be a solution of nickelodithio-oxalic acid.

Its conductivity was measured, and was found to be nearly four times that of an equivalent solution of the barium salt. Moreover, the conductivity of this acid increased with dilution, but decreased steadily on keeping, which would be expected if the acid decomposed into insoluble substances, such as nickel oxalate, sulphur, and carbon monoxide, or into such a feeble electrolyte as hydrogen sulphide.

Strength of solution of barium salt ...	*M*/361	*M*/722
Molecular conductivity	181	196
Strength of solution of nickelodithio-oxalic acid	*M*/722	*M*/1444
Molecular conductivity	736	767

A comparison of the conductivity of this acid with that of equivalent solutions of hydrochloric and sulphuric acids shows that it is a comparatively strong acid, with a conductivity approximately equal to that of sulphuric acid. (The molecular conductivity of sulphuric acid at a dilution of 722 litres is 742.)

Palladiodithio-oxalates.

Potassium palladiodithio-oxalate, $K_2(COS)_4Pd$.—When a solution of palladium chloride is added to a concentrated solution of potassium dithio-oxalate, a yellow, crystalline precipitate separates. This salt is deposited from a hot aqueous solution as yellow, fluorescent prisms:

0·3240 gave 0·1280 CO_2. C = 10·8.
0·3100 „ 0·6970 $BaSO_4$. S = 30·8.
0·4885 „ 0·1250 Pd and 0·5870 K_2PtCl_6. K = 19·2; Pd = 25·6.
$K_2(COS)_4Pd$ requires C = 11·3; K = 18·5; S = 30·5;
Pd = 25·0 per cent.

Barium palladiodithio-oxalate, $Ba(COS)_4Pd,3H_2O$, was prepared by adding barium chloride solution to a solution of the potassium salt. It separates in orange-coloured needles:

0·2915 gave 0·0960 CO_2 and 0·0295 H_2O. C = 8·3; H_2O = 10·1.
$Ba(COS)_4Pd,3H_2O$ requires C = 8·95; H_2O = 10·0 per cent.

Aniline palladiodithio-oxalate, $(C_6H_5{\cdot}NH_3)_2(COS)_4Pd$, separates from a solution of potassium palladiodithio-oxalate on addition of a solution of aniline hydrochloride as a yellow, microcrystalline precipitate:

0·3435 gave 0·4540 CO_2 and 0·0935 H_2O. C = 36·1; H = 3·0.
0·4710 „ 0·0880 Pd. Pd = 18·7.
0·2400 „ 0·4280 $BaSO_4$. S = 24·5.
$(C_6H_5{\cdot}NH_3)_2(COS)_4Pd$ requires C = 36·7; H = 3·06; S = 24·4; Pd = 18·2 per cent.

Solutions of palladiodithio-oxalates have an intense yellow colour, which persists at high dilutions, and is probably due to the formation of a complex anion containing palladium. In agreement with this we find that the ordinary tests for palladium when applied to these solutions fail; thus potassium iodide does not precipitate insoluble palladium iodide, whilst hydrogen sulphide does not cause separation of palladium sulphide.

This complex acid radicle is fairly stable, as the colour is not destroyed by dilute mineral acid, but potassium cyanide decolorises solutions of palladiodithio-oxalates. The following reactions were examined:

Silver nitrate gives a yellow precipitate, which immediately decomposes with evolution of carbon monoxide and formation of silver sulphide.

Mercuric chloride gives a yellow precipitate which blackens on keeping.

Lead acetate gives an orange-red precipitate which darkens after keeping.

Nickel chloride causes formation of a moderately soluble brick-red nickel salt.

Cobalt chloride causes formation of a fairly soluble cobalt salt.

When a solution of palladium chloride in excess is added to one of potassium palladiodithio-oxalate rapid decomposition takes place with separation of palladium sulphide, so that when preparing potassium palladiodithio-oxalate it is important to use an excess of thio-oxalate.

Ferrodithio-oxalates.

When a solution of ferrous ammonium sulphate is added to one of potassium dithio-oxalate, a brownish-purple colour is developed. This colour is due to formation of a complex ferrodithio-oxalate, but owing to the instability of this substance, ferrous sulphide separates when solutions of ferrous ammonium sulphate and potassium dithio-oxalate are mixed, and the isolation of a pure salt proved to be difficult. If, however, dilute solutions were used, it was possible to isolate the sparingly soluble aniline salt by the addition of aniline hydrochloride to the filtered solution.

Aniline ferrodithio-oxalate separated in black needles, which were collected rapidly and dried in a vacuum over sulphuric acid. Even when dry, this salt decomposed slowly, with evolution of hydrogen sulphide and formation of oxanilide, so that no consistent analytical results were obtained, but the following serve to establish the composition of the salt:

0·1525 gave 0·2085 CO_2 and 0·0485 H_2O. $C=37·35$; $H=3·53$.
0·2600 „ 13 c.c. N_2 at 23° and 763 mm. $N=5·67$.
0·1880 „ 0·3780 $BaSO_4$. $S=27·6$.
$(C_6H_5{\cdot}NH_3)_2(COS)_4Fe,H_2O$ requires $C=38·2$; $H=3·58$; $S=25·5$; $N=5·77$ per cent.

Cobaltidithio-oxalates.

When solutions of cobalt salts and potassium dithio-oxalate are mixed, an intense reddish-brown colour results, and this colour is recognisable at dilutions as great as one part of cobalt in 40,000,000 parts of water.

This colour, unlike the corresponding colour for nickel, is not discharged by potassium cyanide or by boiling with moderately strong hydrochloric acid. The colour is therefore due to the formation of a stable complex cobaltidithio-oxalate.

When concentrated solutions of equal weights of cobalt chloride and potassium dithio-oxalate are mixed, an intense reddish-brown colour is developed, and much cobalt sulphide separates. The solution was filtered, and to the filtrate barium chloride solution was added. A reddish-brown, microcrystalline precipitate separated. This was dissolved in hot water, and on cooling very minute, reddish-brown needles separated.

Analysis showed this salt to be *potassium barium cobaltidithio-oxalate*, $BaK(COS)_6Co,4H_2O$.

The potassium was estimated by decomposing the salt by nitric acid; the barium was then removed as barium sulphate, the solution was made alkaline by ammonia, and the cobalt removed as cobalt sulphide. The liquid was then evaporated to dryness, ignited, and the potassium in the residue estimated as platinichloride, but the results obtained were always low:

2·1860 gave 0·7735 $BaSO_4$ and 0·1890 Co. $Ba=20·8$; $Co=8·64$.
0·3545 „ 0·7385 $BaSO_4$. $S=28·6$.
0·6515 „ 0·2655 CO_2 and 0·0715 H_2O. $C=11·1$; $H_2O=11·0$.
0·7485 barium salt gave 0·231 K_2PtCl_6. $K=4·95$.
$BaK(COS)_6Co,4H_2O$ requires $C=10·8$; $H_2O=10·8$; $S=28·78$; $Ba=20·53$; $Co=8·7$; $K=5·83$ per cent.

Potassium cobaltidithio-oxalate, $K_3(COS)_6Co,2H_2O$, was prepared by mixing solutions of equivalent quantities of potassium sulphate and barium potassium cobaltidithio-oxalate, removing the barium sulphate, and evaporating the filtrate until the tripotassium salt separated in very dark brown, stumpy prisms. This was recrystallised from hot water:

0·5015 gave 0·2270 CO_2 and 0·0330 H_2O. C = 12·35; H_2O = 6·58.
0·6890 „ 0·9370 K_2PtCl_6 and 0·0712 Co. K = 21·4; Co = 10·34.
0·5000 „ 1·2120 $BaSO_4$. S = 33·3.
$K_3(COS)_6Co,2H_2O$ requires K = 20·45; C = 12·58; S = 33·54;
Co = 10·31; H_2O = 6·29 per cent.

The behaviour of cobaltidithio-oxalates in solution was studied by means of the freezing point and conductivity of solutions in the case of the corresponding nickel compounds:

0·4140 potassium salt in 20 c.c. water gave $\Delta t - 0{\cdot}22°$. M.W. = 167.
1·0300 in 40 c.c. water gave $\Delta t - 0{\cdot}27°$. M.W. = 172.
Average M.W. = 169·5.
$K_3(COS)_6Co,2H_2O$ requires M.W. = 572.

Hence the salt appears to ionise, giving four ions—$3K'$ and $Co(COS)_6'''$.

Conductivity Experiments.

Dilution	$M/32$	$M/64$	$M/128$	$M/1024$
Molecular conductivity	306	330·6	360	400

Hence:

$$\frac{E_{1024} - E_{32}}{10} = \frac{400/3 - 306/3}{10} = 3{\cdot}12.$$

Cobaltidithio-oxalic acid is therefore tribasic.

Aniline cobaltidithio-oxalate, $(C_6H_5{\cdot}NH_3)_2(COS)_6,2H_2O$, separates as a dark reddish-brown, crystalline precipitate on mixing concentrated solutions of aniline hydrochloride and potassium cobaltidithio-oxalate. The sparingly soluble salt separates from hot water in small, dark brown octahedra:

0·3765 gave 0·5425 CO_2, 0·1190 H_2O, and 0·0300 Co. C = 39·3; H = 3·51; Co = 7·59.
0·3235 gave 15·4 c.c. N_2 at 15° and 779 mm. N = 5·75.
0·3030 „ 0·5800 $BaSO_4$. S = 26·28.
$(C_6H_5{\cdot}NH_3)_3(COS)_6Co,2H_2O$ requires C = 39·08; H = 3·80;
Co = 8·00; N = 5·70; S = 26·0 per cent.

If to a solution of potassium cobaltidithio-oxalate a solution of quinine sulphate is added, quinine cobaltidithio-oxalate separates as a brownish-yellow, microcrystalline precipitate. This salt is apparently quite insoluble in water, so that its formation might be used to estimate quinine.

Lead, silver, nickel, and cobalt salts of cobaltidithio-oxalic acid were not isolated, as they decompose immediately after formation with deposition of sulphides and evolution of carbon monoxide, and, as in the case of nickelodithio-oxalic acid, only those metals which do not form insoluble sulphides give stable salts.

The thermal decomposition of aniline cobaltidithio-oxalate was examined in the manner already described in the case of aniline nickelodithio-oxalate.

This salt decomposes at about 200°, giving oxanilide, aniline, hydrogen sulphide, carbon monoxide, presumably carbonyl sulphide, and a sulphide of cobalt.

I. 0·1620 gave 38·6 c.c. gas at 17° and 754 mm.
After KOH absorption, 13·3 c.c. gas at 17° and 754 mm.

Hence:

164 litres gas per gram-molecule of salt.
55·6 litres carbon monoxide per gram-molecule of salt.

II. 0·5330 gave 0·079 residue = 109 grams per gram-molecule of salt.

III. 162 litres total gas per gram-molecule.
55·7 litres carbon monoxide per gram-molecule.

IV. 161·8 litres total gas per gram-molecule.
54·4 litres carbon monoxide per gram-molecule.

V. 0·6380 gave 0·1430 oxanilide and 0·1320 aniline hydrochloride.

Hence:

150 grams aniline per gram-molecule.
165 ,, oxanilide per gram-molecule.

It was not found possible to estimate carbonyl sulphide in this case as the phenyltrimethylammonium salt is very soluble, and was not obtained pure.

The equation which represents the decomposition of the aniline salt most nearly is:

$$2Co(COS)_6(C_6H_5\cdot NH_3)_3,2H_2O =$$
$$2H_2O + (CO\cdot NH\cdot C_6H_5)_2 + 4C_6H_5\cdot NH_2 + 4H_2S + 5COS + 5CO + Co_2S_3.$$

Products of Decomposition per Gram-molecule of Salt.

	Found.	Calculated.
Carbon monoxide	55·6 litres	55·5 litres
Hydrogen sulphide and carbonyl sulphide	107·4 ,,	99·9 ,,
Aniline	150·0 grams	186·0 grams
Oxanilide	165·0 ,,	120·0 ,,
Cobalt sulphide	109·0 ,,	107·0 ,,

Rhodiidithio-oxalates.

On adding a solution of sodium rhodiichloride to a concentrated solution of potassium dithio-oxalate no apparent change takes place; the addition of barium chloride to the mixed solutions does not cause separation of barium rhodiidithio-oxalate. On warming the solution becomes orange-coloured, and barium chloride now causes separation of a brilliant yellow microcrystalline precipitate. This is soluble in hot water, and separates on cooling as orange-yellow needles of *potassium barium rhodiidithio-oxalate*,

$KBa(COS)_6Rh,4H_2O$:

0·2710 gave 0·0870 $BaSO_4$. Ba = 18·9.
0·6460 „ 0·2470 CO_2 and 0·0680 H_2O. C = 10·43; H_2O = 10·5.
$BaK{\cdot}(COS)_6Rh,4H_2O$ requires Ba = 19·2; C = 10·13;
H_2O = 10·12 per cent.

Aniline Rhodiidithio-oxalate, $(C_6H_5{\cdot}NH_3)_3(COS)_6Rh,H_2O$, separates in orange-red needles when a solution of barium rhodiidithio-oxalate is added to a solution of aniline hydrochloride:

0·2625 gave 0·3610 CO_2 and 0·0840 H_2O. C = 37·5; H = 3·5.
0·2290 „ 0·4270 $BaSO_4$. S = 25·6.
$(C_6H_5{\cdot}NH_3)_3(COS)_6Rh,H_2O$ requires C = 37·7; H = 3·40;
S = 25·2 per cent.

Solutions of rhodiidithio-oxalates have an intense yellow colour, which persists at great dilutions.

The expenses of this investigation have been partly defrayed by grants from the Government Grant Committee of the Royal Society, for which we are glad to make this grateful acknowledgment. We also desire to record our thanks to Professor Pope for kindly supplying us with the salts of palladium and rhodium used in this work.

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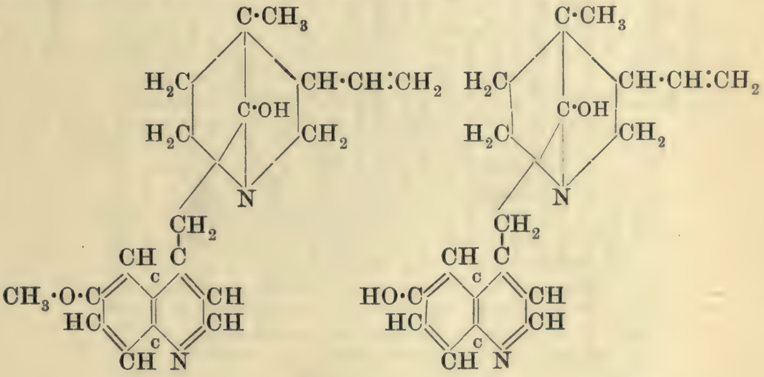
VIII.—*The Absorption Spectra of Quinine, Cupreine, 6-Methoxyquinoline, and 6-Hydroxyquinoline.*

By James Johnston Dobbie and John Jacob Fox.

In a recent paper (Trans., 1911, **99**, 1254) it was shown that the absorption spectra of solutions of cinchonine and quinoline are practically identical, notwithstanding the fact that the molecule of the former has a mass more than twice as great as that of the latter.

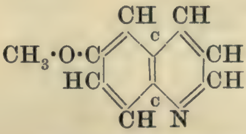
The object of the investigation described in the present paper was to ascertain whether a similar relation exists between the spectra of quinine and cupreine, on the one hand, and those of 6-methoxy- and 6-hydroxy-quinoline, on the other. It was shown in the paper referred to that the quinine spectra are much more complicated than those of cinchonine, and it was assumed that this greater complexity is associated with the presence of a methoxy-group in the quinoline half of the molecule, since no other structural difference is known to exist between the two alkaloids. If this assumption was justified, it was to be expected that the spectra of 6-methoxy- and 6-hydroxy-quinoline would bear as close a relation to those of quinine and cupreine as the spectra of quinoline to the spectra of cinchonine. Our anticipations on this point were fully justified by the results of our investigation.

The structural relations of the four compounds under consideration are exhibited by the following formulæ:

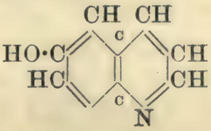


Quinine.

Cupreine.



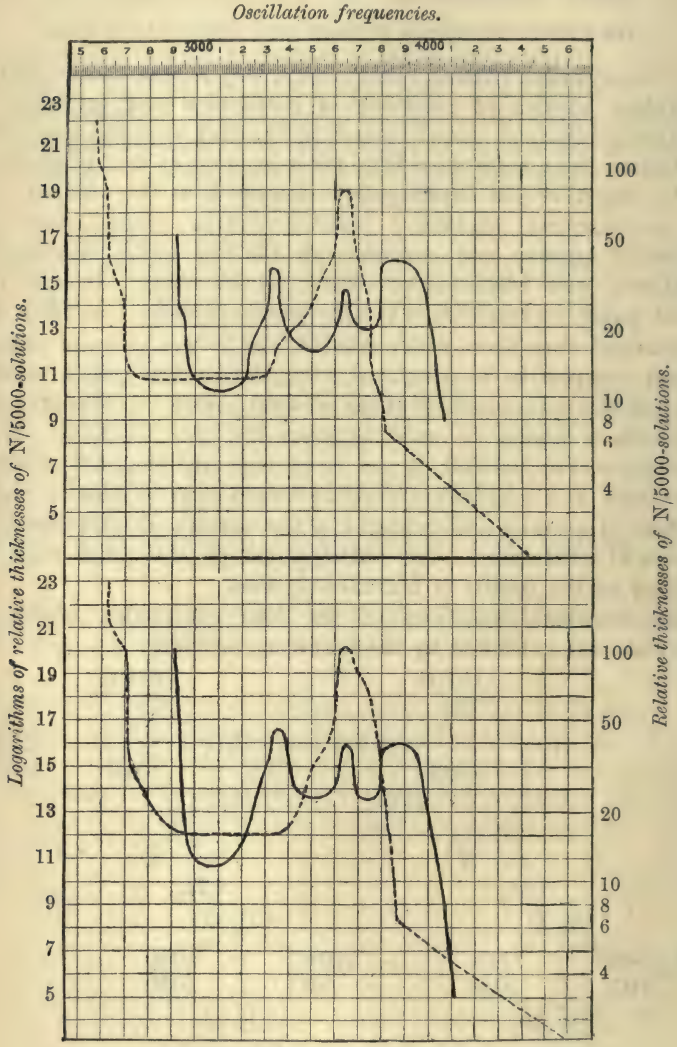
6-Methoxyquinoline.



6-Hydroxyquinoline.

The absorption spectra of solutions in alcohol of these four substances exhibit three bands, the head of the principal band being at 1/λ 3050, and of the others at 1/λ 3500 and 1/λ 3750 respectively. The spectra are almost identical, those of the alkaloids

FIG. 1.



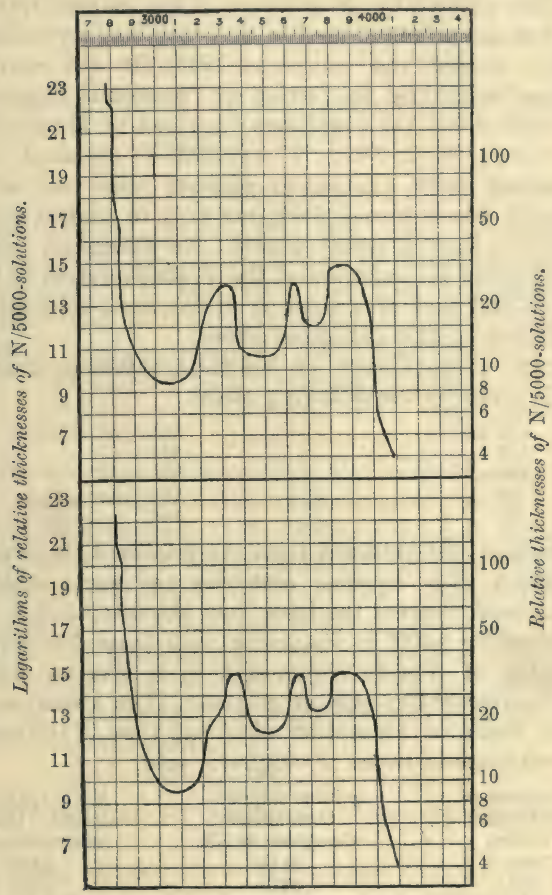
Upper curves : ——— *Quinine in alcohol.*
- - - - - - ,, *hydrochloride.*
Lower curves : ——— 6-*Methoxyquinoline in alcohol.*
- - - - - - ,, *hydrochloride.*

differing from the others only in showing very slightly greater general absorption.*

These spectra are the same as the spectra of the alkaloids in combination with one equivalent of acid. When, however, the amount of acid present is sufficient to combine with both nitrogen

FIG. 2.

Oscillation frequencies.



Upper curve: *Cupreine in alcohol.*
Lower ,, 6-*Hydroxyquinoline in alcohol.*

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* The curves of quinine now published were drawn from photographs of a larger number of thicknesses of solution than the curves on p. 1260 (*loc. cit.*), and therefore show the shape of the bands more completely. The position and extent of the bands, however, is in no way affected.

atoms of the quinine, the spectrum is similar to that of 6-methoxyquinoline hydrochloride, although the difference in general absorption is slightly more marked than in the alcoholic solutions.

It is clear from an inspection of the curves (Figs. 1 and 2) that the absorption spectra of quinine and cupreine, as well as those of cinchonine, are due to the quinoline portion of the molecule, and are but little affected by the presence of the reduced rings.

The 6-hydroxyquinoline used in this work was crystallised several times from alcohol, and melted at 194°. It was converted into 6-methoxyquinoline by the action of potassium hydroxide and methyl iodide under the conditions described by Skraup (*Monatsh.*, 1882, **3**, 544; 1885, **6**, 762). The viscous oil obtained in this way when distilled under diminished pressure came over as a faintly yellow liquid, which turned dark, not only in contact with the air, but also when kept in closed vessels. No difference, however, was observed between the spectrum of the *N*/1000-solution of the freshly distilled oil and that of a solution of the same strength after the oil had undergone this change of colour.

The range of distillation of 6-methoxyquinoline under varying pressure is given by the following table:

740 mm.	304—305° (Skraup)
310 ,,	254°
220 ,,	236—237°
50 ,,	193° (Skraup)
35 ,,	186° ,,

The cupreine was obtained from recrystallised cupreine sulphate by treatment with aqueous ammonia and warm ether and subsequent crystallisation of the base from absolute alcohol.

An interesting point in connexion with these substances is that the sulphate of 6-methoxyquinoline is, as Skraup pointed out, strongly fluorescent like quinine sulphate. The accompanying table shows the limits of absorption obtained from *N*/100-solutions of the two sulphates in excess of sulphuric acid:

Thickness of N/100-solution in mm.	Quinine sulphate. Continuous absorption to 1/λ.	Methoxyquinoline sulphate. Continuous absorption to 1/λ.
60	2419	2486
50	2419	2486
40	2419	2519
30	2486	2519
25	2486	2519
20	2486	2519
15	2486	2519
12	2519	2519
8	2519	2559
6	2519	2614

It is noteworthy that the physiological properties of quinine are not shared by 6-methoxyquinoline. The conclusion appears to be justified that the action of quinine as a febrifuge is not due alone to the presence of the methoxy-group, the only point in which it differs structurally from cinchonine, but to the presence in the same molecule of this group and the reduced part which is common to quinine and cinchonine.

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IX.—*Latent Heats of Vaporisation of Mixed Liquids. Part II.*

By DAN TYRER.

IN the previous paper (Trans., 1911, **99**, 1633) a method was described for determining the latent heats of vaporisation of binary mixtures of liquids. It was pointed out that a mixture of two liquids has two latent heats of vaporisation, which have been termed "latent heat at constant pressure" and "latent heat at constant composition," and denoted by the symbols L_p and L_c respectively. These two magnitudes are simply related in a manner shown as follows:

Take a large quantity of the mixture, the composition of which in terms of one of the constituents is x. Let its boiling point under the normal atmospheric pressure be T. Allow 1 gram of the liquid to evaporate at the constant temperature T. The heat absorbed is $(L_p)_x$. Let the composition of the vapour be y. Separate the vapour from the liquid, and compress it completely to liquid at the constant temperature T. The heat evolved in this process is $(L_c)_y$. Now allow the 1 gram of liquid thus produced to mix with the original liquid. Let the heat of mixture be H. Clearly we have from the first law of thermodynamics the relation:

$$(L_p)_x = (L_c)_y + H.$$

It must be noted that all the terms of this equation refer to the constant temperature T.

Knowing, then, L_p and H, we can calculate L_c for a liquid the composition of which is the same as the composition of the vapour which boils off from a mixture the latent heat of which at constant pressure is L_p.

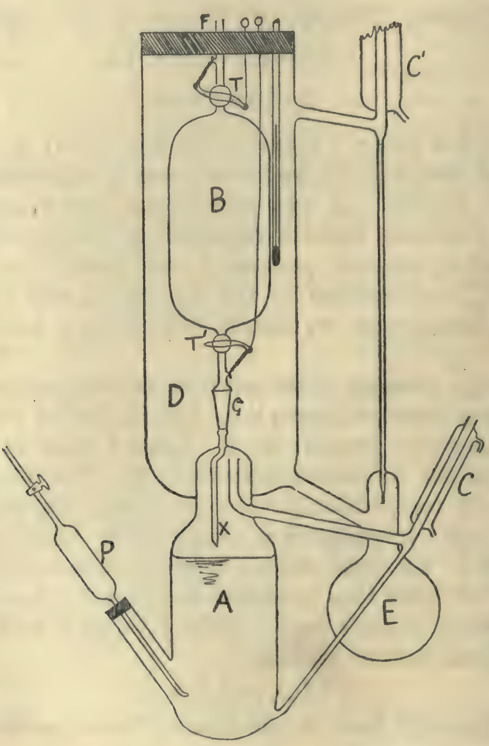
In the present work the compositions of mixed vapours which are in equilibrium with mixed liquids of known compositions at their boiling points have been determined for the cases previously investigated, and complete results for two new cases have also been recorded.

EXPERIMENTAL.

Determination of Composition of Vapour in Equilibrium with Boiling Liquid of Known Composition.

The method employed to determine the composition of the vapour which boils off from a mixture of two liquids of known composition consists in principle in determining the density of the vapour, and from this calculating the composition by assuming the validity of the additive law for mixed vapours.

FIG. 1.



The mixture of liquids to be investigated is placed in the vessel *A* (Fig. 1), where it is boiled. The vapour which comes off passes into the upper portion of *A*, into the condenser *C*, and then returns as liquid into *A* again. *A* is connected by the tube *X* and ground-glass joint to the vessel *B*. *B* is provided with two taps, *T* and *T′*, which can be opened or closed from the outside by the aid of springs. The vessel B is heated in the vapour jacket D to a temperature somewhat higher than the boiling point of the mixture. The vapour in the jacket D comes from the liquid boiling in the flask E, and after passing through D it is condensed in C', and returns to the boiling flask. In carrying out an experiment, the vessel B containing air is placed in position with the taps T and T' closed. The liquids in A and E are boiled, and after the temperature has become constant the tap T' is first opened and then T, and B is filled with vapour from A by attaching the end of the tube F to an aspirator. After all the air in B has been displaced, the tap T is closed, and after a few minutes tap T' is also closed. A sample of the boiling liquid in A is then taken off in the pipette P for analysis. The temperature in D is read to a tenth of a degree, and the barometric pressure noted. The vessel B is then taken out and cleaned and weighed. Air is then drawn through it, and it is then again weighed and filled with air at a known temperature and pressure. From the data thus obtained and from the known volume of B, the density of the mixed vapour for the particular temperature and pressure recorded can be calculated. The densities of the vapours of the pure constituents are determined in a similar manner, and then assuming the additive law of mixtures to hold for mixed vapours, the composition of the mixture of vapours is easily calculated. The sample of liquid drawn off in the pipette is transferred to a pyknometer, and its specific volume determined. From its specific volume its composition can be calculated in a manner explained in the previous paper. All the data required are now obtained. It remains only to plot the experimental results on squared paper, and to read off from the smoothed curve values at even points.

As the amount of liquid in A is fairly large (about 250 c.c.), and the vapour space above it relatively small, the composition of the liquid will be fairly constant throughout the experiment, and the sample abstracted in the pipette will have the proper composition; also, in the passage of the vapour from the vessel A to B the arrangement of the apparatus obviates any possibility of it condensing, which would of course entirely vitiate the results. The vapour is drawn off from as near the surface of the boiling liquid as possible, so as to be sure we are dealing with vapour arising directly from the boiling liquid, and not from re-condensed liquid adhering to the walls of the vessel. In regard to the assumed validity of the additive law for mixed vapours, the error of this assumption will be negligible. With the liquids themselves the additive law is only slightly violated, and with the mixed vapours the deviation from the law will be still smaller.

The compositions of the vapours in equilibrium with the liquid mixtures have been determined in the following cases:

(1) Carbon tetrachloride and ether.
(2) Chloroform and benzene.
(3) Carbon tetrachloride and ethyl acetate.
(4) Ethyl bromide and benzene.

The latent heats at constant pressure in the first two cases were recorded in the previous paper. From the now measured compositions of their mixed vapours, their latent heats at constant composition have been determined. For particulars of the method of determining latent heats at constant pressure the previous paper (*loc. cit.*) must be consulted.

Results.

Latent Heats at Constant Pressure of Mixtures of Carbon Tetrachloride and Ethyl Acetate

The carbon tetrachloride used in these experiments was obtained from Kahlbaum's pure material by washing repeatedly with water, drying over calcium chloride and phosphoric oxide, and then distilling, the first and last portions being rejected; 500 c.c. distilled over without the boiling point changing more than 0·07°. It had a specific volume at 23·13° of 0·63002, boiled at 75·92°/745 mm., and had a latent heat (at 75·92°) of 47·29 calories. This result for the latent heat was calculated from the value 46·85 at 77·75° found in previous experiments by the aid of the formula $LM = KT\log\frac{D_L}{D_V}$, where L is the latent heat, M the molecular weight, D_L and D_V the densities of liquid and vapour respectively at T degrees, and K is a constant.

The ethyl acetate was obtained by the further purification of Kahlbaum's pure material. At 23·15° it had a specific volume of 1·11495, and boiled at 76·50°/745 mm.

Latent Heat of Pure Ethyl Acetate.—Three consecutive determinations were made, and the following results obtained:

Pressure.	Temperature.	Latent heat.
755 mm.	76·95°	87·67 calories.
747 ,,	76·51	88·21 ,,
743 ,,	76·47	88·02 ,,

These results calculated to the temperature 76·50° give as a mean value 87·97 calories. Results by other observers are: Ramsay and Marshall (*Phil. Mag.*, 1896, [v], **41**, 38), 88·1; Kahlenberg (*J. Physical Chem.*, 1901, **5**, 215, 284), 90·9; Brown (Trans., 1903, **81**, 987), 88·37.

Latent Heats at Constant Pressure of Mixtures.—The results given in the following table were read off from a smoothed curve of experimental values.

Composition of liquid. (Per cent. of CCl_4.)	Temperature of boiling (745 mm.).	Latent heat at constant pressure.
0	76·50°	87·97 calories.
10	76·06	83·70 ,,
20	75·56	79·60 ,,
30	75·10	75·45 ,,
40	74·74	71·35 ,,
50	74·35	67·35 ,,
60	74·07	63·25 ,,
70	74·10	59·20 ,,
80	74·34	55·22 ,,
90	74·89	51·20 ,,
100	75·92	47·29 ,,

Latent Heats at Constant Pressure of Mixtures of Ethyl Bromide and Benzene.

The ethyl bromide used in these experiments was prepared by adding bromine to a mixture of alcohol and red phosphorus. To free it from ether, which appeared to be the chief impurity, it was boiled, and the vapour passed through a slightly acid solution of potassium permanganate at 100°. It was then washed, dried over calcium chloride and phosphoric oxide, and fractionated. About 700 c.c. distilled over without the boiling point changing more than 0·15°. It had a specific volume of 0·69163 at 25°, and boiled at 38·38°/760 mm.

The pure benzene was the same as that used in the previous experiments described in the first paper.

Latent Heat of Pure Ethyl Bromide.—Three experiments gave the results:

Pressure.	Temperature.	Latent heat.
749 mm.	37·98°	59·70 calories.
749 ,,	38·02	59·89 ,,
761 ,,	38·42	60·05 ,,

Mean result at 38·38°/760 mm. is 59·88 calories.

Wirtz (*Ann. Phys. Chem.*, 1890, **40**, [iii], 438) obtained the result 60·37.

Latent Heats of Mixtures at Constant Pressure.—The results given in the following table were read off from a smoothed curve of experimental results:

Composition of liquid. (Percentage of ethyl bromide).	Temperature of boiling at 760 mm.	Latent heat at constant pressure.
0	80·25°	94·35
10	74·86	86·60
20	70·00	79·80
30	65·39	74·1
40	60·84	69·9
50	56·52	66·7
60	52·59	64·6
70	48·78	63·0
80	45·10	61·85
90	41·49	60·85
100	38·38	59·88

Composition of the Vapour Boiling off from a Mixture of Known Composition.

The following results have been read from smoothed curves of experimental values:

	Composition of vapour.			
Composition of liquid.	Carbon tetrachloride and ether. (Percentage of carbon tetrachloride.)	Chloroform and benzene. (Percentage of chloroform.)	Carbon tetrachloride and ethyl acetate. (Percentage of carbon tetrachloride.)	Ethyl bromide and benzene. (Percentage of ethyl bromide.)
0	0	0	0	0
10	1·72	13·6	10·7	26·6
20	4·28	27·2	21·1	46·8
30	8·0	40·6	31·2	61·4
40	12·7	53·0	41·2	72·0
50	18·5	65·0	51·1	80·4
60	25·4	75·0	60·4	86·4
70	34·6	83·0	70·4	91·0
80	47·2	90·0	80·4	94·6
90	67·8	96·1	90·2	97·6
100	100	100	100	100

Latent Heats at Constant Composition.

From the foregoing results we can calculate by aid of the equation $(L_p)_x = (L_c)_y + H$ the latent heats at constant composition. We must, however, know H, the heat of mixture. Now with normal liquids the heat developed on mixing is very small, and possibly negligible, but as this was not certain, a few rough experiments were made to test it.

In the case of carbon tetrachloride and ethyl acetate the composition of the vapour is so near to that of the liquid that the heat of mixture H is almost immeasurably small. H, it must be remembered, is the heat developed when 1 gram of liquid, the composition of which is the same as the composition of the vapour boiling off from a large quantity of a mixture of known composition, is added to this latter large mass of liquid. The value of H in the case of carbon tetrachloride and ethyl acetate is less than 0·01 calorie. To about 150 c.c. of a mixture of chloroform and benzene containing 49 per cent. of the former were added 20 c.c. of a mixture containing 64 per cent. of chloroform, which is approximately in the same proportion as the compositions of liquid and vapour. The total rise in temperature was only 0·032°, and calculating from the known specific heat of the mixture, the approximate value of H was found to be 0·08 calorie. In another experiment H was found to be about 0·12 calorie. In this case, therefore, we can consider H to be negligible. In a similar manner it has been proved that H can be disregarded as negligibly small in the other two cases. We can therefore write the above equation:

$$(L_p)_x = (L_c)_y.$$

By plotting the values of $(L_p)_x$ against the compositions y, and reading off from the curve, values for L_c at even points, the following tables of results have been obtained:

Carbon Tetrachloride and Ether.

Composition. (Percentage of carbon tetrachloride.)	Temperature.	Latent heat at constant composition. Calories.
0	34·75°	86·44
10	41·35	83·1
20	44·84	79·4
30	48·98	75·7
40	53·09	71·9
50	57·16	68·3
60	61·44	64·6
70	65·54	60·6
80	69·73	56·5
90	73·70	51·9
100	77·75	46·85

Chloroform and Benzene.

Composition. (Percentage of chloroform.)	Temperature.	Latent heat at constant composition. Calories.
0	80·65°	94·35
10	79·86	91·1
20	79·03	87·9
30	78·13	84·6
40	77·15	81·4
50	75·95	78·2
60	74·60	75·0
70	72·84	71·6
80	70·48	68·3
90	67·00	64·4
100	61·45	59·29

Carbon Tetrachloride and Ethyl Acetate.

Composition. (Percentage of carbon tetrachloride.)	Temperature.	Latent heat at constant composition. Calories.
0	76·50°	87·97
10	76·05	84·10
20	75·58	80·05
30	75·12	75·95
40	74·72	71·95
50	74·35	67·90
60	74·10	63·75
70	74·10	59·60
80	74·29	55·50
90	74·83	51·40
100	75·92	47·29

Ethyl Bromide and Benzene.

Composition. (Percentage of ethyl bromide.).	Temperature.	Latent heat at constant composition. Calories.
0	80·25°	94·35
10	78·33	91·6
20	76·30	88·6
30	74·13	85·3
40	71·75	81·9
50	69·10	78·3
60	65·86	74·6
70	61·76	70·9
80	56·72	67·1
90	49·90	63·5
100	38·38	59·88

Discussion of Results.

The latent heat of a mixture at constant pressure does not appear to bear any simple relation to the composition. It is not by any means an additive property, as might have been expected. This conclusion has already been established in the cases previously investigated, and the results for the two fresh cases investigated in the present work support this conclusion.

In regard to the latent heat at constant composition, this appears to approximate closely to a linear function of the composition. This is shown graphically by the curves in the figure. It will be observed that with the exception of the line for carbon tetrachloride and ether, which is slightly curved, the lines are practically straight. The ethyl bromide + benzene and the benzene + chloroform lines are just a little curved at one extremity.

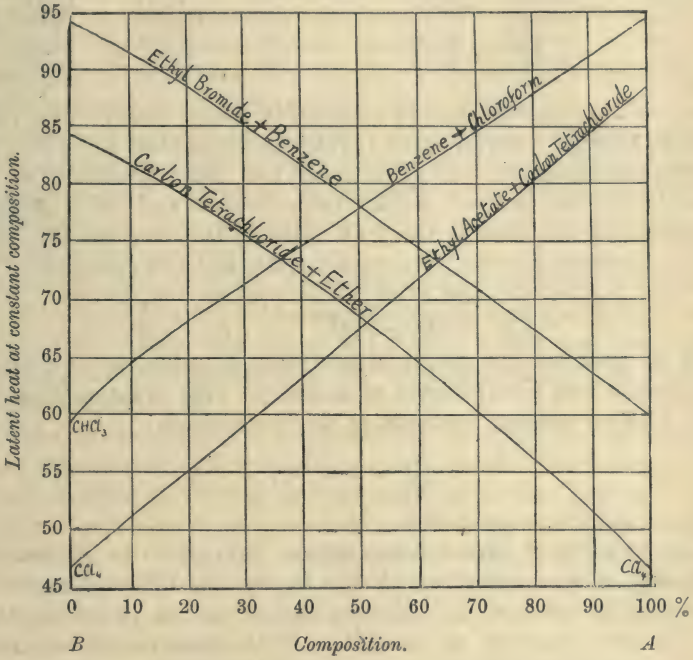
We may therefore regard the latent heat of a liquid mixture at constant composition as approximately a linear function of the composition.

The well known relation of Trouton:

$$\frac{LM}{T} = \text{constant},$$

where L is the latent heat, M the molecular weight, and T the absolute boiling point, is not applicable, as was shown in the previous paper, to latent heats of mixtures at constant pressure, but holds for latent heats at constant composition. For M there must be taken the mean molecular weight of the molecules in the mixture (see Trans., 1911, **99**, 1644).

FIG. 2.



In the following tables are given values of L_cM/T calculated from this equation:

Carbon tetrachloride and ether.

$C.$	$M.$	$\frac{L_cM}{T}.$
0	74·08	20·81
10	78·30	20·70
20	82·65	20·65
30	87·73	20·62
40	93·46	20·61
50	100·45	20·78
60	107·53	20·77
70	116·28	20·81
80	126·58	20·87
90	138·89	20·79
100	153·84	20·55

Chloroform and benzene.

$C.$	$M.$	$\frac{L_cM}{T}.$
0	78·05	20·83
10	80·95	20·84
20	83·86	20·94
30	87·23	21·02
40	90·60	21·06
50	94·56	21·19
60	98·52	21·26
70	103·24	21·38
80	107·96	21·47
90	113·67	21·53
100	119·39	21·06

Carbon tetrachloride and ethyl acetate.

C.	M.	$\frac{L_cM}{T}$.
0	88·06	22·16
10	92·59	22·31
20	96·92	22·26
30	101·67	22·18
40	106·91	22·12
50	113·67	22·22
60	119·21	21·89
70	126·49	21·72
80	134·70	21·53
90	144·40	21·34
100	153·84	20·85

Ethyl bromide and benzene.

C.	M.	$\frac{L_cM}{T}$.
0	78·05	20·85
10	80·33	20·94
20	82·94	21·04
30	85·32	20·96
40	88·05	20·92
50	90·97	20·82
60	94·08	20·71
70	97·41	20·63
80	100 99	20·55
90	104·84	20·62
100	109·00	20·96

As will be observed, the relation holds fairly closely. The value of L_cM/T must, however, vary slightly in those cases for which the pure constituents do not give quite the same constant, as, for example, in the case of carbon tetrachloride and ethyl acetate. However, we can take as the true value of the constant the mean of the constants for the pure constituents, and the equation:

$$\frac{L_c}{T} \cdot \cdot \frac{100\, M_A M_B}{CM_B + (100 - C)M_A} = \tfrac{1}{2}\left(\frac{L_A M_A}{T_A} + \frac{L_B M_B}{T_B}\right)$$

could be used for calculating latent heats of mixtures at constant composition with a fair degree of accuracy. This equation gives the ratio L_c/T as a linear function of the composition:

$$\frac{L_c}{T} = a + bC,$$

where a and b are constants.

The validity of Trouton's equation for mixtures proves the normality of those mixtures, that is to say, the different molecules of the liquids retain their individual existence when mixed together, and do not dissociate or associate. With mixtures of associated liquids, like water and the alcohols, to which it is hoped to extend these investigations, the above relations will probably not hold, the values of L_c/T perhaps showing maxima or minima.

In conclusion, the author desires to state that a portion of the expense of this work has been defrayed by a Research Grant from the Chemical Society, and for which the author expresses his thanks.

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X.—*The Methane Equilibrium.*

By John Norman Pring and Dorian Macefield Fairlie.

It has been found that hydrogen and carbon when in the purest condition combine directly to form methane at temperatures between 1200° and 1500°; ethylene at all temperatures above 1200° (although not in any considerable quantity below about 1500°); and acetylene at all temperatures above 1700° (Pring, Trans., 1910, **97**, 498; Pring and Fairlie, *ibid.*, 1911, **99**, 1796).

Ethylene and acetylene were found to unite readily with hydrogen to give methane at all temperatures above about 700°.

A careful investigation of the equilibrium between carbon, hydrogen, and methane at different temperatures will be of particular value with regard to its application to the calculation of specific heats at temperatures where direct measurements cannot be made with any accuracy.

This application of thermodynamics to the calculation of chemical equilibria from heat data has been developed and verified by van't Hoff, Nernst, Haber, and others, but there are very few cases where accurate data are available to enable the extension of these formulæ to high temperatures.

In the work hitherto carried out on the synthesis of methane under atmospheric pressure, it was not possible to measure the precise equilibrium values, as the whole apparatus was not at a uniform temperature, and traces of ethylene formed at the higher temperature of the carbon would combine with hydrogen in zones of lower temperatures and give methane, thus raising the quantity of this latter to an amount greater than the equilibrium value at the higher temperature.

It is not practicable to use a reaction vessel, the walls of which can be heated to temperatures above 1200° and remain gas-tight.

A calculation of the methane equilibrium at high temperatures has been made by Mayer and Altmayer (*Ber.*, 1907, **40**, 2134) on the basis of experimental measurements made between 250° and 850°, and by making use of thermodynamical deductions. The formula as applied in this particular case is expressed by Haber * as follows:

$$\log_e K = \frac{Q_0}{RT} - \frac{\sigma \log_e T}{R} - \frac{\sigma_1 T}{R} + \frac{k}{R}.\dagger$$

K is here the reaction constant, or $\frac{p\text{-CH}_4}{p\text{-(H}_2)^2}$, Q_0 the heat of reaction at absolute zero, $\sigma + \sigma_1 T + \sigma'' T^2$ the sum of the specific heats, at constant pressure, of the substances disappearing ($C + 2H_2$) and that appearing (CH_4) in the reaction, the value for methane being taken as negative. T is the absolute temperature, and k an indeterminate constant. On examining experimentally the equilibrium at temperatures between 250° and 850°, the value of k was found to be 21·1. Taking 18,500 as the heat of formation of methane at absolute zero, the above equation took the form:

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* "Thermodynamics of Technical Gas Reactions." 1908. p. 345.

† The term $\frac{1}{2}\sigma_1{}'' T^2$ is omitted from this equation.

$$\log K = \frac{4050}{T} - 3{\cdot}027 \log T - 0{\cdot}0006424 T + 4{\cdot}617.$$

At 1200° this gives as the equilibrium ratio of methane to hydrogen the value 0·07 per cent.

It is obvious, however, that the variables in this equation are not known with sufficient precision to enable its application at high temperatures; for instance, in the above calculation, the term σ_1 in the specific heat of methane was omitted as the value is unknown, and for σ, the value 9·106 found by Wüllner between 0° and 200° was used. A large departure will thus be produced at the higher temperatures. A still greater discrepancy than the above arises from taking for the heat of formation of methane a value which is based on data relating to amorphous carbon. Diamond is known to be the stable form of carbon at the ordinary temperature, and graphite at higher temperatures. In consequence of this, graphite has at the ordinary temperature a heat of combustion 2840 calories (per gram-atom) less than the value for amorphous carbon (Berthelot, *Compt. rend.*, 1889, **108**, 1144).

The difference at absolute zero can be calculated from Kirchhoff's law, according to which:

$$Q_0 = Q_T - T(C_{(f)} - C_{(p)}),$$

where Q_0 and Q_T denote the heat of transformation of amorphous carbon into graphite at the temperatures 0° and T° (absolute). $C_{(f)}$ and $C_{p)}$ are the mean specific heats of carbon and graphite respectively.

The atomic heat of amorphous carbon is given by Kunz (*Ann. Physik*, 1904, [iv], **14**, 327) as $2{\cdot}0094 + 0{\cdot}00173T$, and the value for graphite as determined by Behn (*ibid.*, 1900, [iv], **1**, 264) is $0{\cdot}0 + 0{\cdot}0075T$ (compare also Nernst, *ibid.*, 1911, [iv], **36**, 395). Q_0 is therefore equal to 2506 cals., and the heat of formation of methane from graphite will consequently be 16,000 cals. at absolute zero. When the unstable substance, amorphous carbon, takes part in a gaseous equilibrium, a false value will be produced and maintained for some time.

This has indeed been observed by Schenck and Heller (*Ber.*, 1905, **38**, 2139), who studied the equilibrium in some reactions in which carbon in different modifications takes part.

In the case of the equilibrium between carbon dioxide, carbon monoxide, and carbon in different modifications, the reduction of carbon dioxide was greatest when amorphous carbon was used. A similar result was obtained in the reaction between iron oxide, carbon, and carbon monoxide; thus, in this case, at 550° the pressure of carbon monoxide obtained when in "metastable equilibrium" was, with amorphous carbon, 59 mm., diamond, 22 mm., and graphite, 12 mm.

In the present work an investigation was made of the reaction between carbon and hydrogen at high gaseous pressures, with a view to find the equilibrium values at high temperatures, and incidentally to obtain some idea of the effect of pressure on the progress of the synthesis. Since the formation of methane proceeds according to the equation $C + 2H_2 = CH_4$, it follows, from the law of mass action, that $\frac{p\text{-}CH_4}{p\text{-}(H_2)^2} = k$, a constant at any given temperature. It is seen from this that an increase of pressure of n times will increase the ratio of methane to hydrogen n times; further, if in a series of experiments a constant value is obtained for k at different pressures, we have an indication that this represents the true equilibrium constant.

The objections, enumerated above, to the determination of the methane equilibrium in the form of apparatus used in the earlier work (*loc. cit.*) at atmospheric pressure were largely overcome in these experiments at high pressures.

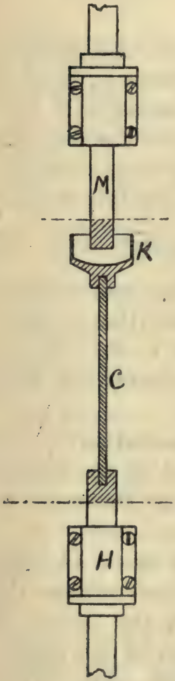
It was found in the preliminary experiments made at high pressures that in these cases the formation of methane attains the equilibrium value much more rapidly, even when the carbon is used in absence of any catalyst, and the disturbance of the equilibrium due to the formation of ethylene will be very much diminished on account of the rapid cooling of the gaseous product by the water-cooled steel walls of the reaction vessel.

Methane is, of course, stable in larger amounts the lower the temperature, so that apart from the slight disturbance through the traces of ethylene formed, the quantity of methane finally obtained will correspond with the equilibrium at the temperature of the heated carbon.

Part I.—Experiments with Pressures up to 100 *Atmospheres.*

Apparatus.—This series of experiments were carried out with a pressure furnace designed by Hutton and Petavel (*Phil. Trans.*, 1908, *A*, **207**, 428). This apparatus was constructed for investigating reactions produced by the electric arc at high pressures. For the present work it was adapted for heating carbon in the form of a rod, uniformly, and at definitely controlled and measured temperatures between 1100° and 2100°. The carbon (*C*, Fig. 1), which was 6 to 8 mm. diameter and 8 to 12 cm. long, was inserted in graphite end-pieces, the bottom one of which was clamped by one of the brass electrode holders (*H*). The top graphite piece was turned in the form of a cup (*K*), which was filled with pure graphite powder. A graphite rod (*M*) was fastened in the top clamp, and after the furnace top had been fastened down and the pressure admitted, this electrode could be lowered by screwing down (compare Hutton and Petavel, *loc. cit.*), and a satisfactory electrical connexion established between the carbon rod and the top electrode by means of the graphite in the cup. The temperature was estimated by means of a Wanner optical pyrometer, by sighting through the glass window mounted in the furnace walls.

FIG. 1.



In a number of the earlier experiments, before admitting the hydrogen, the furnace was exhausted and filled with methane, so as to introduce a small percentage of this gas and accelerate the attainment of the equilibrium value.

Preparation of Materials.

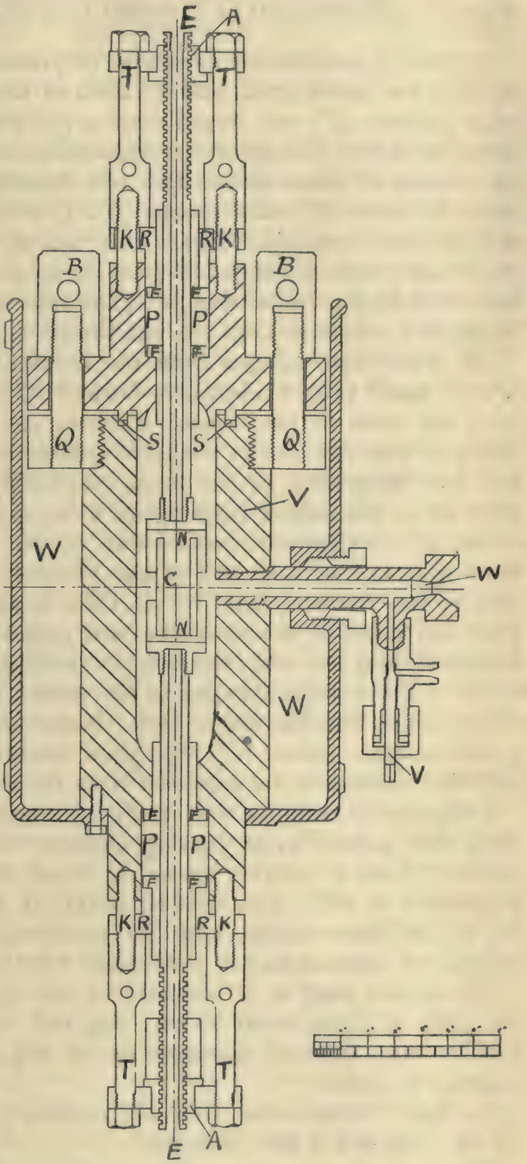
Hydrogen.—This was prepared by acting on zinc (prepared electrolytically) with sulphuric acid (compare Hutton and Petavel, *J. Soc. Chem. Ind.*, 1904, **23**, 88), and after washing, the gas was compressed in steel bottles. On analysis it was found to contain 98·0 per cent. of hydrogen and 2·0 per cent. of nitrogen.

Carbon.—This was used in the form of rods of retort carbon, usually 8 mm. in diameter and about 10 cm. long. They contained originally about 2 per cent. of ash (oxides of iron, silicon, etc.) and about 0·2 per cent. of combined hydrogen. They were purified by supporting with water-cooled electrodes in a large glass tubular flask, heating electrically to 1400—1500° in a stream of chlorine, and then in hydrogen in the same manner.

When the carbon was used in presence of a catalyst (platinum or palladium), a layer of either of these metals was coated on the carbon by electro-deposition from a chloride solution before heating in hydrogen.

Methane.—This was prepared by decomposing commercial aluminium carbide with water, passing the gas through ammoniacal cuprous chloride to remove acetylene and hydrogen sulphide, and then liquefying with liquid air. After evaporation, the gas was collected over water in a large holder of 20 litres capacity. In some experiments carbon was used which had received no purification treatment beyond heating a short time in the furnace in hydrogen at a high pressure. In all these cases, however, it was estimated that the amount of combined hydrogen present as impurity always corresponded with a quantity of methane well below that subsequently produced in the synthesis.

FIG. 2.



Part II.—Experiments at Pressures from 100 *to* 200 *Atmospheres.*

In these experiments a new form of pressure furnace of smaller capacity was constructed, and is shown in diagram in Fig. 2. The inner cylinder (V) was forged from a piece of nickel steel of high tensile strength. The electrodes consisted of steel tubes ($E\ E$), which were cooled by water circulation, and contact with the carbon was made by means of nickel clamps ($N\ N$), which were brazed to the ends of these electrodes. The carbon rods or tubes (C) were always fitted into graphite end-pieces (not shown in the diagram), which were held in the nickel clamps. [The tube or rod (C) was always longer and narrower than the one shown in the figure.]

The electrodes emerged from the furnace at the stuffing boxes ($P\ P$). Small tubes of ebonite or fibre ($F\ F$) insulated the electrodes from the walls of the latter. Asbestos cord mixed with a little tallow or wax was used as the packing material for the boxes ($P\ P$), and was compressed by the brass rings $R\ R$, which were forced down on to the ebonite rings by six bolts, as at $K\ K$. The outward thrust of the electrodes was secured by the bolts ($T\ T$), of which there were two at each end of the furnace. The top part of the furnace was fastened down by six bolts as at $B\ B$, and a gas-tight joint was made by means of the lead spigot $S\ S$. By opening the bottom stuffing-box and removing the packing, the bottom electrode could be lifted while clamped to the carbon rod and top electrode, and removed with the furnace top. Water circulation was provided in the annular jacket W. The glass window, X, was placed at a sufficient distance to be protected from the heat of the carbon.

Temperature readings were made by means of the light radiated from the carbon, after passing through the window and being reflected from a mirror placed in front of the window at an inclination of 45°. The window could, as a rule, be safely used up to 200 atmospheres, and the remainder of the furnace was capable of withstanding a pressure of 1000 atmospheres.

The carbon used at C consisted of amorphous retort carbon in the form of tubes about 12 cm. long and either 20 mm. external and 15 mm. internal diameter or 15 mm. external and 9 mm. internal diameter.

In some experiments rods of (Acheson) graphite were used, 12 cm. long and 9 mm. diameter.

With amorphous carbon, after mounting in the furnace, a partial purification was obtained by giving a preliminary heating to about 1400° in hydrogen at about 50 atmospheres pressure, and then liberating and renewing the gas. As mentioned above, the quantity of combined hydrogen present as impurity was always well below the large amount of methane subsequently synthesised.

The capacity of the furnace was about 750 c.c. In experiments at 100 atmospheres, where, say, 10 per cent. of methane was formed, this would involve the synthesis of about 7½ litres (at N.T.P.) of this hydrocarbon.

On account of the corrosion of the carbon, it was not as a rule possible to use the same carbon in more than one experiment. In the course of a large amount of work where carbon rods and tubes have been heated electrically at atmospheric pressure under different conditions, it has been found that the heating of the carbon always takes place with great uniformity throughout the whole length when the amorphous variety is used. This is on account of the negative temperature-coefficient of resistance. With graphite, however, the temperature falls a little near the cold ends of support.

Analysis of Gases.—The gas obtained in these experiments, which contained from 1 to 20 per cent. methane, was analysed in the Sodeau apparatus. After complete removal of carbon monoxide and any unsaturated hydrocarbons, a fractional combustion of the hydrogen by means of oxygen in presence of palladium-black was usually applied (compare Pring and Fairlie, Trans., 1911, **99**, 1796). The saturated hydrocarbon could then be estimated and identified by the relation found between the contraction after exploding with oxygen, and the volume absorbed by potassium hydroxide solution. In all these cases methane was, at all temperatures, found to be the only saturated hydrocarbon produced.

In an experiment carried out at 1275°, an examination was made for traces of ethylene by circulating a large quantity of the gas (25 litres) through a tube cooled in liquid air. Most of the methane was thus condensed, together with the whole of any ethylene present. This liquid was then allowed to evaporate slowly, and the last portion was passed through a tube containing carefully purified cocoanut charcoal. A further fractional separation was here carried out (compare *ibid.*, p. 1802), and the last portion of 50 c.c. on analysis was found to contain 0·51 c.c. ethylene, or 0·002 per cent. of the total gas. As the amount of methane formed was 21 per cent., the ratio of ethylene to the latter is lower than that found at atmospheric pressure (*ibid.*, p. 1806), but the method of fractionation used could only serve for a rough measure of the actual quantity of ethylene present.

On account of the difficulty of accurately estimating nitrogen, the following method was adopted. In experiments in Part I, the hydrogen on being analysed several times was found to give a mean value of 2·0 per cent. for the nitrogen content. In Part II the hydrogen used was commercial electrolytic, and was found to contain 0·2 per cent. nitrogen as the mean result of several analyses. These mean values were taken in considering the results of subsequent experiments.

Change of Pressure.—The formation of methane, proceeding according to the equation $C + 2H_2 = CH_4$, is accompanied by a contraction of volume equivalent to the volume of methane formed. In these experiments this was equivalent to a change of pressure. Consequently, by reading the pressure indicated by the gauge, the course of the reaction could usually be followed, and the attainment of equilibrium recognised. With the first type of pressure furnace (Part I) it was not possible to keep the enclosure quite gas-tight when used for long intervals on account of the gradual heating of the electrodes by the heavy currents used. This softened the packing in the stuffing-boxes, and caused leakage. With the second type of furnace this trouble was obviated by the use of the water-cooled electrodes. In this case, however, a considerable time was necessary for the mean temperature of the enclosure to become constant on account of the large quantity of metal present. In many experiments samples of gas were withdrawn during the heating at different intervals, and analysed, in order to ascertain when equilibrium had been reached.

The results of all successful experiments which were carried out are tabulated below in the order of temperature. All those at pressures below 100 atmospheres were conducted in the first type of furnace, as described in Part I (p. 93), and those at pressures of 100 atmospheres and above in the second type (Part II, p. 96).

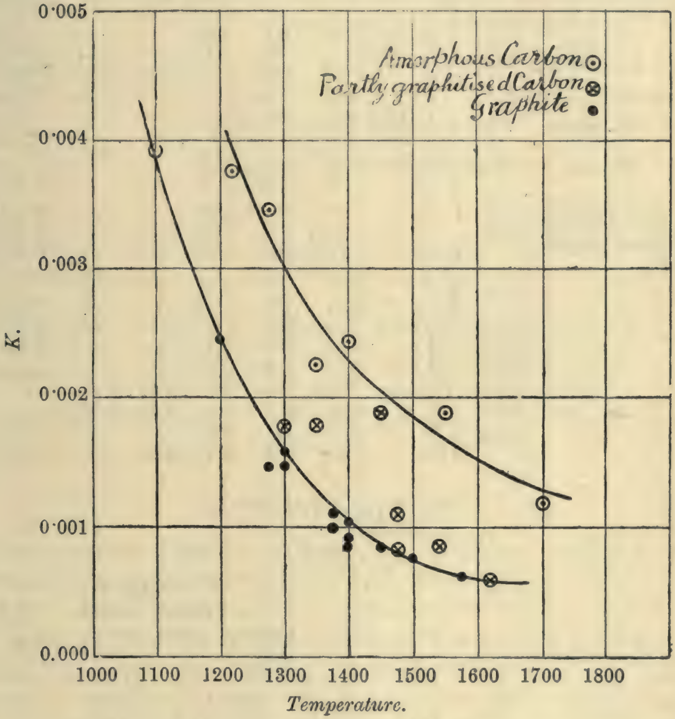
It is seen in all cases that where amorphous carbon was used an amount of methane was given which gradually fell on continuing the heating, and finally approached a stationary value, the same as that given in the first place with graphite.

This fall in the quantity of methane always took place *pari passu* with the gradual change of amorphous carbon into graphite, and was more rapid the higher the temperature.

When the carbon was purified by heating in chlorine for a few hours at 1400° to 1500°, it was observed to have undergone a partial transformation into graphite, and when use was made of this the quantities of methane were always intermediate between those obtained with unpurified amorphous carbon and graphite. The presence of platinum or palladium on the surface of the carbon, on the other hand, did not appear to accelerate the change into graphite.

In table I below are given the values for amorphous carbon, which in some cases was impure, and in others had been partly purified in chlorine at a temperature too low to cause any appreciable change into graphite. In table II are given the experiments done with graphite. This was either Acheson graphite or else carbon which had previously been heated for a long interval at a high temperature in hydrogen, or else had been purified at a high temperature in chlorine so as to cause transformation into graphite. The carbon in all these cases was practically pure.

FIG. 3.



In table III are given the experiments with carbon which, by previous heating or purification, had become partly transformed into graphite. The results are also plotted in the form of curves (Fig. 3), where the ordinates denote the equilibrium constants, and the abscissæ the temperatures.

The values obtained in experiments at temperatures above about 1700° do not represent equilibrium quantities, as the methane in these cases is formed chiefly by the reaction of ethylene and acetylene in the cooler parts of the vessel. The results at these higher temperatures are consequently not plotted in the figure.

TABLE I.

Amorphous Carbon. First Time of Use.

Nature of carbon.	Temperature.	Time.	Pressure (atms.).	Percentage composition.				$K = \frac{p\text{-CH}_4}{p\text{-(H}_2)^2}$.
				CO.	CH_4.	C_2H_2.	C_2H_4.	
Purified. Pt. coated	1100°	0	—	—	4·10	—	—	—
		2½ hrs.	20	1·1	6·35	—	—	0·00390
Impure. Pt. coated	1220	0	—	—	4·1	—	—	—
		3 ,,	18	1·4	5·6	—	—	0·00376
Partly purified ………	1275	3 ,,	100	0·25	21·5	—	0·002	0·00359
Impure. Pt. coated	1350	1 hr.	166	0·6	18·5	—	—	0·00173
		2½ hrs.	153	0·7	20·9	—	—	0·00224
Purified. Pt. coated	1400	0	—	—	4·35	—	—	—
		1¾ ,,	18	0·92	3·86	—	—	0·00245
Same carbon as above (To show effect of progressive graphitisation) …………	1400	1½ ,,	19	1·0	2·35	—	—	0·00138
		3 ,,	18·5	1·4	1·98	—	—	0·00120
		4½ ,,	17·5	3·3	1·28	—	—	0·00084
Impure ………………	1550	0	—	—	4·65	—	—	—
		1½ ,,	21	1·5	3·49	—	—	0·00188
,, ………………	1620	20 mins.	20	3·7	1·0	—	—	0·00058
,, . Pt. coated	1700	1 hr.	15	7·5	1·4	nil	—	0·00120
,, ……………	1775	4 hrs.	117	1·6	9·0	nil	0·1	—
,, ………………	1950	7 mins.	24·5	3·4	2·4	0·29	0·44	—
,, ………………	2050	7 ,,	23	2·8	2·8	0·74	1·10	—
Purified………………	2100	0	—	—	5·5	—	—	—
		15 ,,	25	5·5	2·6	0·25	?	—

TABLE II.

Graphite.

Nature of graphite.	Temperature.	Time.	Pressure (atms.).	Percentage composition of gas.		$K = \frac{p\text{-CH}_4}{p\text{-(H}_2)^2}$
				CO.	CH_4.	
Acheson …………………	1200°	2½ hrs.	105	0·0	17·5	0·00244
Carbon graphitised by heating. Pt. coated.	1275	0	—	—	2·38	—
		25 mins.	37	1·6	4·23	0 00133
		1¾ hrs.	32	2·4	4·02	0·00147
Carbon graphitised by heating. Pd. coated.	1300	½ hr.	37	0·6	4·69	0·00120
		1 ,,	35·5	1·0	4·55	0·00146
Acheson …………………	1300	1 ,,	117	0 0	11·2	0·00126
		2¼ hrs.	106	0·0	12·6	0·00158
Carbon graphitised by heating ………………	1375	1 hr.	28	1·4	2·5	0·00100
Acheson …………………	1375	3 hrs.	115	0·2	10·6	0·00117
Graphitised by heating. Pd. coated.	1400	0	—	—	2·4	—
		¼ hr.	46	0·1	3·90	0·000945
		1¼ hrs.	46	0·2	4·29	0·00103
Graphitised by heating. Pt. coated.	1400	0	—	—	1·6	—
		1½ ,,	50	1·3	3·99	0·00089
Same carbon as above …	1400	0	—	—	1·6	—
		¾ hr.	55	0·5	4·24	0·00080
		1¾ hrs.	48	1·0	3·71	0·00089

TABLE II (*continued*).

Nature of graphite.	Temperature.	Time.	Pressure (atms.).	Percentage composition of gas.		$K = \frac{p\text{-CH}_4}{p\text{-(H}_2)^2}$.
				CO.	CH_2.	
Carbon graphitised by heating. Pt. coated.	1450	0	—	—	2·3	—
		20 mins.	47	2·0	3·39	0·000843
		1 hr.	44	2·4	3·01	0·000746
Carbon graphitised by heating. Pt. coated.	1500	0	—	—	1·8	—
		½ ,,	55	0·8	3·96	0·00080
		1 ,,	52	1·2	3·62	0·00077
Carbon graphitised by heating. Pt. coated.	1575	0	—	—	—	—
		12 mins.	52	0·7	2·94	0·00063
		1½ hrs.	44	1·0	2·46	0·00062

TABLE III.

Partly Graphitised Carbon.

Nature of carbon.	Temperature.	Time.	Pressure (atms.).	Percentage composition of gas.		$K = \frac{p\text{-CH}_4}{p\text{-(H}_2)^2}$.
				CO.	CH_4.	
Purified	1300°	1¾ hrs.	7	7·3	1 0	0 00178
Impure. Pt. coated......	1350	2 ,,	11·5	5·75	1·71	0·00178
Purified. ,, ...	1450	1¼ ,,	136	0·3	17·1	0·00186
Impure. ,, ...	1475	1¼ ,,	177	0·3	16·7	0·00137
		4½ ,,	155	0·3	11·9	0·00101
Impure........................	1475	1¼ ,,	200	0·05	13·1	0·00087
		3¼ ,,	200	0·25	12·4	0·00083
Impure........................	1540	1½ ,,	183	0·05	12·0	0·000860

Results and Conclusions.

The reaction between carbon and hydrogen resulting in the formation of methane was found to proceed with increased velocity at high gaseous pressures. Using carbon in the form of a compact rod or tube, and either in presence or absence of a catalyst, the equilibrium stage was reached in about two hours, when the temperature was 1200—1300°, and the pressure 30 to 50 atmospheres. Above 1400°, equilibrium was reached in about fifteen minutes under the same conditions. At 200 atmospheres the reaction was still more rapid.

These results indicate the probability that carbon in a fine state of division would at still higher pressures combine with hydrogen with extreme rapidity, as the reaction is exothermic. In this way, the preparation of methane might most conveniently be carried out on a large scale. No saturated hydrocarbon but methane is formed at any temperature between 1100° and 2100° or pressure up to 200 atmospheres. The relative amount of methane produced increased with the pressure to the extent demanded by the law of mass action as applied to the reaction $C + 2H_2 = CH_4$. According to this, the value $\frac{p\cdot CH_4}{p\cdot(H_2)^2}$ should be constant at any given temperature.

In all experiments at pressures varying from 10 to 200 atmospheres, a value which was constant within the limits of experimental error was always obtained for this ratio at any particular temperature and when the same modification of carbon was used.

In some experiments where an amount of methane in excess of this value was added to the gas beforehand, decomposition took place until the same final value was obtained. Consequently, this represents the true equilibrium constant.

The amount of methane which at atmospheric pressure is in equilibrium with hydrogen and graphite is at 1200° equal to 0·24 per cent., and at 1500°, 0·07 per cent. For amorphous carbon the "metastable equilibrium" values are 0·36 per cent. at 1200° and 0·21 per cent. at 1500°.

The values for amorphous carbon are not so definite as those for graphite on account of the gradual transformation which the former undergoes into the latter at the temperatures used in these experiments.

The results definitely show, however, that the change of free energy in the transformation of carbon into graphite increases rapidly in the range of temperature between 1200° and 1600°.

It follows from this by the application of Kirchhoff's law relating to heats of reaction and specific heats, that the mean specific heat of amorphous carbon must be much higher than that of graphite between 0° and 1200°, and that this difference increases with the temperature. This shows that the values obtained for the specific heat of carbon by Kunz (*Ann. Physik,* 1904, [iv], **14**, 327) and of graphite by Weber (*Ber.*, 1872, **5**, 303) are relatively not applicable at these temperatures. According to these values, in which the specific heat of graphite is at all temperatures above 100° higher than amorphous carbon, it would follow from Kirchhoff's law that the latter modification of carbon is at all temperatures more stable than the former. Hence, the specific heat of carbon must increase with temperature more rapidly than that of graphite.

The values for the equilibrium constants obtained in this work will probably serve for a more accurate determination of the relative specific heats of carbon and graphite, and of carbon, hydrogen, and methane at these high temperatures, than is possible by any direct method of measurements.

This calculation is possible from the formula of van't Hoff showing the relation between the equilibrium constant, temperature, and heat of reaction, and by applying the law of Kirchhoff.

The formation of traces of ethylene has been observed at a temperature as low as 1275° (0·002 per cent. of the total gas when the pressure was 100 atmospheres). This quantity could not exert any noticeable effect on the methane yield, which in this particular experiment amounted to 21·5 per cent.

At temperatures between 1800° and 2100°, no appreciable effect was exerted by high pressures on the yield of acetylene and ethylene when the results are compared with those obtained in earlier work (*loc. cit.*) at atmospheric pressure.

We are indebted to Dr. R. S. Hutton for his kind assistance in the early stages of this work. Part of the expense incidental to the construction of the pressure furnace has been borne by a grant from the Research Fund of the Royal Society.

We are also indebted to Professor Rutherford for the continued provision he has made for carrying on this investigation.

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XI.—*The Solubility of Electrolytes in Aqueous Solutions. Part II. Solubility of Oxalic Acid in Other Acids.*

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IN a previous communication (Trans., 1911, **99**, 1132) an account was given of experiments on the solubility of chlorides and nitrates in aqueous solutions of the corresponding acids. A certain quantitative relation between the solubility of the salt and the concentration of acid was shown to exist, and it was found that the molecular volumes of the components of the solution could be regarded as independent of the relative concentrations. The present work, which was undertaken with the view of examining the behaviour of mixed acids in the light of these conclusions, deals with saturated solutions of oxalic acid in aqueous nitric acid and in aqueous hydrochloric acid, and also of β-naphthalenesulphonic acid in aqueous hydrochloric acid. As will be seen, the results with oxalic acid display several peculiarities which partly obscure the relation to the earlier results, but which in themselves are of interest.

EXPERIMENTAL.

The determinations of solubility and density were carried out, as before, at 30·0°. The technique was identical with that previously described. In analysis, the concentration of oxalic acid was measured, in both sets of experiments, by precipitating the calcium salt, dissolving it in dilute sulphuric acid, and titrating with *N*/10-potassium permanganate. Hydrochloric acid was estimated by adding excess of *N*/10-silver nitrate, and titrating the filtrate with *N*/10-ammonium thiocyanate. In solutions containing nitric acid or β-naphthalenesulphonic acid, the total acidity was measured, and the concentration of the constituent in question was obtained by difference.

The materials used were of the purest commercial brands, except in the cases of the strongest nitric acid and of the sulphonic acid. The former was obtained by distillation from a mixture of fuming nitric acid and sulphuric acid in a current of carbon dioxide, and was slightly yellow. β-Naphthalenesulphonic acid was obtained from the impure commercial article by fractionally precipitating and extracting the lead salt, which was then dissolved in boiling water and decomposed with dilute sulphuric acid. From the resulting solution, crystals were obtained on saturating the liquid with hydrogen chloride. After being dried in a vacuum over quicklime and sulphuric acid, the substance was pure and anhydrous; but it decomposed to a certain extent when dissolved in water, imparting a brown colour to the solution.

In the tables of results, the symbols used are as follows:

S=specific gravity of the solution at 30·0° (water=0·9957); a=gram-molecules of "solvent acid" (HCl or HNO_3) per litre of solution at 30°; b=gram-molecules of saturated "dissolved acid" per litre of solution at 30°; w=gram-molecules of water per litre of solution at 30°.

TABLE I.

Oxalic acid—Nitric acid.

S.	*a.*	*b.*	*w.*
1·0594	0	1·479	51·15
1·0648	0·478	1·268	50·84
1·0932	1·606	1·039	49·60
1·1172	2·453	0·933	48·50
1·1666	4·224	0·790	45·74
1·2582	7·600	0·661	39·63
1·3075	9·59	0·639	35·51
1·3584	11·84	0·696	30·17
1·3938	13·62	0·847	25·15
1·4060	14·12	0·966	23·48
1·4319	15·59	1·114	19·03
1·4443	16·92	0·840	16·42
1·4819	20·84	0·524	6·38
1·4863	21·23	0·531	5·20
1·4886	21·57	0·548	4·07
1·4917	21·63	0·553	4·01

Oxalic acid—Hydrochloric acid.

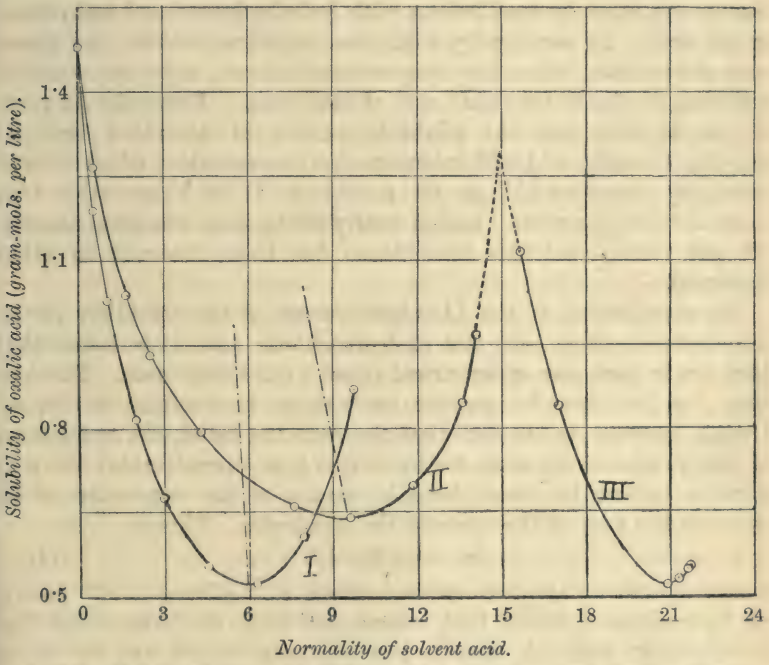
S.	*a.*	*b.*	*w.*
1·0594	0	1·479	51·15
1·0561	0·503	1·190	51·62
1·0577	0·970	1·032	51·34
1·0654	1·939	0·821	50·83
1·0757	2·959	0·675	50·10
1·0957	4·528	0·555	48·33
1·1165	6·026	0·525	46·89
1·1494	7·907	0·607	44·49
1·1843	9·68	0·871	41·52

TABLE I (*continued*).

β-Naphthalenesulphonic acid—Hydrochloric acid.				β-Naphthalenesulphonic acid—Hydrochloric acid.			
S.	*a.*	*b.*	*w.*	*S.*	*a.*	*b.*	*w.*
1·1925	0·000	3·263	28·20	1·1115	4·017	0·762	44·49
1·1653	1·291	2·470	33·25	1·1197	7·232	0·089	46·21
1·1553	1·826	2·117	35·69	1·1569	9·88	0·063	43·21

Discussion of Results.

(*a*) *Solubility.*—The accompanying figure shows the concentration-relations for both of the oxalic acid series. The reflex nature of the curves indicates that there are conflicting influences at work in the solutions. Some insight into the nature of these influences is gained chiefly from the case of nitric acid.



I. $HCl - H_2C_2O_4,2H_2O$. II. $HNO_3 - H_2C_2O_4,2H_2O$. III. $HNO_3 - H_2C_2O_4$.

In the first place, it was proved by special quantitative tests that nitric acid at 30° has no decomposing action on dissolved or on solid oxalic acid, even with solutions of 16*N*-nitric acid which were left for a week in the thermostat.

Secondly, analysis of the crystals precipitated from the solutions proved that those which had been deposited from nitric acid of concentration less than about 15*N* were pure dihydrate of oxalic acid, containing only a trace of mother liquor, whilst the solid deposited from solutions of higher nitric acid content consisted of crystals of anhydrous oxalic acid, also practically free from mother liquor. In these analyses it was necessary to carry out direct determinations of oxalic acid as well as of total acidity, since the equivalent weights of nitric acid and of hydrated oxalic acid are identical. In the case of hydrochloric acid solutions, the range of concentration was not so wide, and the crystals were found to be dihydrate throughout.

There is thus a transition point, at which nitric acid solution and vapour can exist in equilibrium with both hydrated and anhydrous oxalic acid. In conformity with the analytical results, the phase rule shows that, when the temperature is fixed, only one kind of solid can be stable on either side of this point. From the diagram it can be seen that the solubility curves of hydrated and of anhydrous oxalic acid will intersect at a concentration of nitric acid equal to about 14·8*N*, or 66 per cent. It is noteworthy that "constant boiling point" acid is nearly of the same strength, namely, 68 per cent.; and this coincidence has been observed in other instances.

On examination of the U-shaped curves of the solubility of the dihydrate in nitric acid and in hydrochloric acid, it is found that they are in each case symmetrical about a rectilinear axis. Further, they can be shown by graphic methods to be portions of ellipses. Owing, however, to the fact that the axes are tilted, the application of the quadratic equation for an ellipse is not practicable; but it is possible to test the conic form by means of the expression which involves the sum of the roots of the quadratic. This is:

$$a_1 + a_2 = k_1 - k_2 b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1),$$

where a_1 and a_2 are two concentrations of "solvent acid" (nitric or hydrochloric) which both correspond with the same solubility, b, of oxalic acid. k_1 and k_2 are constants which can be evaluated from two pairs of such conjugate points. Hence it is possible to calculate the value of acid-concentration which is conjugate with a given experimental value; and it may then be compared with the figure read from the curve. Table II shows the result of such a comparison; and it is seen that the agreement is satisfactory.

It should be added that similar results are obtained by the use of concentrations per kilogram of water instead of those per litre of solution.

TABLE II.

Oxalic acid—Nitric acid.

a_1.	a_2 cal.	a_2 read.
1·61	14·07	14·3
2·45	13·93	13·98
4·22	13·10	13·10
7·60	10·57	10·80
9·59	8·73	8·92
11·84	6·10	6·10
13·62	3·32	3·38
14·12	2·04	2·04

$k_1=22·53$
$k_2=\ 6·59$

Oxalic acid—Hydrochloric acid.

a_1.	a_2 cal.	a_2 read.
1·94	9·45	9·43
2·96	8·56	8·56
4·53	7·11	7·05
6·03	5·64	5·7
7·91	3·68	3·68
9·68	1·67	1·68

$k_1=12·14$
$k_2=\ 0·92$

An examination of other solubility data reveals the fact that these results are not alone in possessing a conic form. The curve for the solubility of potassium fluoride in aqueous hydrofluoric acid of varying strength (Ditte, *Compt. rend.*, 1896, **123**, 1282) is practically a hyperbola, and the figures may be calculated by means of equation (1) with very fair accuracy. So also the results of Engel (*Compt. rend.*, 1887, **104**, 913) for potassium nitrate in nitric acid solution are in harmony with the equation, although not as closely as in the former case.

In each of these instances, the minimum and subsequent rise of solubility is known to be due to increasing quantities of soluble acid-salt in solution, in accordance with the effect of addition of acid on the equilibrium: salt + acid $\rightleftarrows$ acid-salt. In the present cases, no such combination could be detected, but the cause of their similarity to the above instances may be traced to the result of competition between dissolved oxalic acid and solvent acid for water-molecules, whereby hydrated oxalic acid in solution is partly converted into the anhydrous compound, so bringing about a rise of total solubility; and with sufficient concentration of solvent acid, the anhydrous acid will reach a precipitating concentration, the transition point of the solids thus being attained.

A further case was investigated, namely, *β*-naphthalenesulphonic acid in saturated solution in aqueous hydrochloric acid. As has been mentioned, this sulphonic acid does not yield pure solutions; hence only sufficient experiments were carried out to show that the trend of the curve differs radically from those which represent the oxalic acid cases, and that it resembles the curves of the salt-acid type. Analysis of the deposited solid, after it had been left for six weeks over a quantity of the anhydrous preparation, indicated that it contained two molecular proportions of water of crystallisation.

(*b*) *Specific Gravity and Volume.*—In the case of the salt-acid solutions, the results were shown to be in harmony with the assumption that the molecular volumes of the components are independent of the relative concentrations; and the equation:

$$\alpha a + \beta b + \gamma w = 1000 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

was accordingly found to express the results with accuracy. α, β, and γ are the volumes in question.

In each of the cases now under discussion, the same equation applies, as the example given in table III shows. In this, which refers to hydrochloric acid solutions of oxalic acid, the found values of w, the water concentration, are compared with those calculated from the eperimental figures for a and b, the constants having been evaluated from three points.

TABLE III.

Water Concentrations: $HCl–H_2C_2O_4,2H_2O$ *series.*

Calc.	51·10	51·55	51·34	50·83	50·10	48·45	46·95	44·49	41·61
Found	51·15	51·62	51·34	50·83	50·10	48·33	46·89	44·49	41·52

It is of interest to note that the molecular solution volume appears to vary largely in different cases; for instance, that of oxalic acid in the solutions of the anhydrous compound in nitric acid is 58; in the dihydrate mixtures with nitric acid, it is 115, whilst in the hydrochloric case it is 55. At present no satisfactory explanation is forthcoming of these and of similar variations which are observed with other substances.

Summary.

It has been shown that the solubility at 30° of oxalic acid dihydrate in aqueous nitric acid, and also that in aqueous hydrochloric acid, each passes through a minimum as the concentration of the solvent acid is increased. In nitric acid solutions, the solubility ceases to rise at a concentration at which the solid in equilibrium is converted into the anhydrous form; it then falls to a second minimum. The U-shaped curves expressing the solubilities of the dihydrate are portions of conic sections, and resemble in this way certain other solubility results.

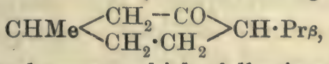
The equation involving the assumption of constant molecular volume in solution has been again found to be valid.

I wish to thank Professor James Walker for the interest which he has taken in the work.

THE UNIVERSITY OF EDINBURGH.

XII.—*The Alcohols of the Hydroaromatic and Terpene Series. Part II. The Menthols Corresponding with Optically Inactive Menthone.*

By **Robert Howson Pickard** and **William Oswald Littlebury.**

A hydroaromatic ketone having the constitution of *p*-menthane-3-one,  $CHMe<\begin{matrix}CH_2-CO\\CH_2\cdot CH_2\end{matrix}>CH\cdot Pr^{\beta}$, should exist in two modifications —*cis* and *trans*—which, following the usual nomenclature, may be conveniently named menthone and *iso*menthone without assigning to either name any special configuration. Further, as these ketones contain asymmetric carbon atoms, each ketone should correspond with a pair of optically active isomerides. When the carbonyl group is reduced to the secondary carbinol group, the possible number of optically inactive isomerides is increased to four, and the number of optically active isomerides to eight. Thus, from theoretical considerations, two optically inactive menthols corresponding with menthone should exist, and each of these should be capable of resolution into a pair of optically active isomerides, whilst in a similar manner the existence of four optically active *iso*menthols derived from *iso*menthone may be expected. In this paper these isomerides are named according to a nomenclature based on that used by Aschan (" Chemie der alicyklischen Verbindungen," Braunschweig, 1905) and that used by Kipping and Tutin (Trans., 1904, **85**, 65) to describe the isomeric menthylamines obtained by them. Thus the two ketones are named menthone and *iso*menthone, whilst the alcohols corresponding with each of them are named menthol and *neo*menthol, and *iso*menthol and *neoiso*menthol respectively; but it must not be assumed that these prefixes as used by Kipping and Tutin for the menthylamines are now used to denote the menthols which exactly correspond with them in configuration.*

Several menthones and menthols are described in the literature, some being natural products, whilst others have been prepared in the laboratory. The investigation of these compounds is a matter of considerable difficulty, owing firstly to the ease with which as a result of tautomerism the ketones pass over into their isomerides, and secondly, to the difficulty of separating the alcohols. The slight knowledge concerning the relationship between these compounds is well summarised by Kondakoff (*J. pr. Chem.*, 1905, [ii],

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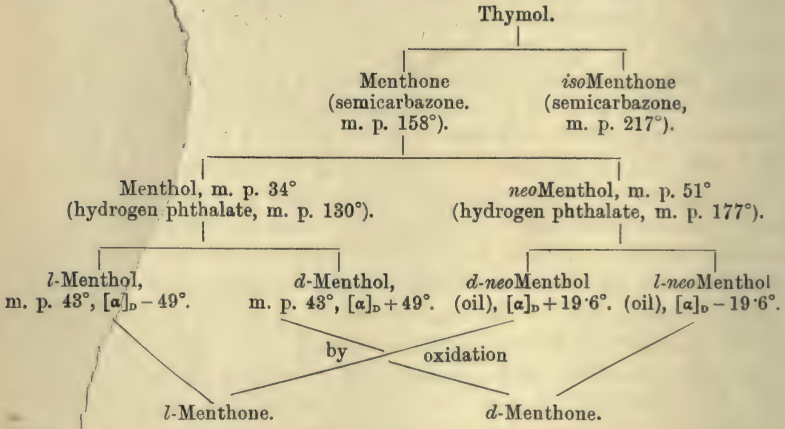
* There is, however, no doubt from experiments of Wallach (*inter alia*, *Annalen*, 1907, **353**, 323), which have been repeated by the present authors, that *l*-menthol possesses the same configuration as *l*-menthylamine.

72, 185). Little further is known on this subject, except the description of the *d-iso*menthone by Beckmann (*Ber.*, 1909, **42**, 846), who has been the principal investigator in this field, and whose researches will be referred to later.

The starting point of the present authors' investigations was a series of papers by Brunel (*Compt. rend.*, 1905, **140**, 252, *et seq.*), who showed that by means of the Sabatier and Senderens reaction it was possible to reduce thymol with hydrogen in the presence of finely divided nickel. The "hexahydrothymol" thus obtained is a mixture, and was, in fact, imperfectly and partly separated by Brunel himself. This material appeared to the present authors as likely to contain the various optically inactive menthols, and, as methods had been worked out in this laboratory for the resolution of optically inactive alcohols, it was hoped that an investigation of this material would throw some light on the relationship between the various optically active menthones and menthols. The present paper contains a description of the relationship which exists between all the menthols corresponding with optically inactive menthone; the second part of the work, namely, the separation and resolution of the menthols corresponding with *iso*menthone, is in hand.

The following diagram indicates the results obtained:


Thymol.
Menthone (semicarbazone. m. p. 158°).
*iso*Menthone (semicarbazone, m. p. 217°).
Menthol, m. p. 34° (hydrogen phthalate, m. p. 130°).
*neo*Menthol, m. p. 51° (hydrogen phthalate, m. p. 177°).
l-Menthol, m. p. 43°, $[\alpha]_D - 49°$.
d-Menthol, m. p. 43°, $[\alpha]_D + 49°$.
*d-neo*Menthol (oil), $[\alpha]_D + 19{\cdot}6°$.
*l-neo*Menthol (oil), $[\alpha]_D - 19{\cdot}6°$.
by oxidation
l-Menthone.
d-Menthone.

The product of the reduction of thymol is a very complex mixture, and in addition to menthones and menthols contains 1-methyl-3-*cyclo*hexanol. Unchanged thymol is removed by washing with a solution of sodium hydroxide, and the mixture heated with phthalic anhydride for ten hours at 115° to convert the alcohols into hydrogen phthalic esters, which are then removed by washing with a dilute solution of sodium carbonate. The ketones remaining, when treated with semicarbazide in the usual manner, yield a mixture of two semicarbazones, which have widely differing solubilities in alcohol—the one, which is nearly insoluble in cold alcohol, melts at 217°, probably corresponds with *iso*menthone, and has previously been obtained by Wallach (*Annalen*, 1908, **362**, 272); the more soluble one melts at 158°, has been prepared by Brunel (*loc. cit.*, p. 749), and corresponds with menthone.

Fractional crystallisation of the hydrogen phthalic esters from acetic acid yields two pure products—the less soluble one melts at 177°, the more soluble one melts at 130°, and has previously been obtained by Brunel (*loc. cit.*). These can also be separated in the form of their magnesium salts, that of the hydrogen phthalate (m. p. 177°) being soluble in water, whilst that of the ester (m. p. 130°) is only sparingly soluble in water, and crystallises readily from warm alcohol.

The ester of higher melting point is probably identical with a hydrogen phthalate prepared by Enklaar (*Ber.*, 1908, **41**, 2086) from a cyclic alcohol formed by the "Sabatier" reduction of geraniol, and, when hydrolysed, it yields an optically inactive menthol, which melts at 51°. This menthol—"*neo*menthol," according to the nomenclature now adopted—has previously been isolated by Beckmann (*J. pr. Chem.*, 1897, [ii], **55**, 30) from the mixture obtained when the phenylcarbamate of natural *l*-menthol was hydrolysed by sodium ethoxide at 150°.

The ester with the lower melting point gives, when hydrolysed, inactive menthol, which, when quite pure, melts at 34°. This is probably identical with the β-thymomenthol * of Brunel (*loc. cit.*) and with the menthol obtained by Kremers (*Amer. Chem. J.*, 1896, **18**, 762) by the reduction of a synthetical menthone.

Menthol is thus characterised by its melting point (34°), by the hydrogen phthalate, which melts at 130°, by the hydrogen succinate, which melts at 85—86°, and by the phenylcarbamate, which melts at 102—104°. When oxidised by Beckmann's method (*J. pr. Chem.*, 1897, [ii], **55**, 14) it yields menthone, which by the usual methods forms an oxime melting at 80°, and a semicarbazone melting at 158°. It can be resolved into its optically active components by methods used by the authors in the case of *iso*borneol (Trans., 1907, **91**, 1973). After many recrystallisations from acetone (or alcohol) of the cinchonine or brucine salt of the hydrogen phthalic ester, the nearly pure lævorotatory isomeride of the menthol can be obtained, whilst the corresponding dextrorotatory form can be obtained in a similar manner from the cinchonidine salt of the hydrogen succinate. It was found that, whilst the benzoate of the optically inactive menthol is an uncrystallisable oil, the benzoates of the optically active isomerides crystallise readily from warm alcohol. The optically active menthols were thus completely purified by the crystallisation of the benzoates. The lævorotatory isomeride was found to be identical in melting point and specific rotation with the *l*-menthol found in essential oils, whilst the dextrorotatory isomeride had the same melting point and a specific rotation equal to, but of opposite sign to, the natural product. The specimens of *l*- and *d*-menthol thus obtained had quite different odours.

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* The product (named by Brunel) α-thymomenthol is probably not a homogeneous substance.

*neo*Menthol (m. p. 51°) forms a hydrogen phthalate, which melts at 177°, a hydrogen succinate, which melts at 67—68°, and a phenylcarbamate, which melts at 114°, and when oxidised yields menthone, as proved by the formation of an oxime and semicarbazone * identical with those obtained from the menthone formed in the oxidation of menthol (m. p. 34°). A very tedious fractional crystallisation from acetone of the brucine salt of the hydrogen phthalate gave a small amount of a product from which *d-neo*menthol with $[\alpha]_D^{18}$ $+19{\cdot}7°$ was obtained. By crystallisation of the quinine salt of the hydrogen succinate, an ester was obtained, which, when hydrolysed, gave *l-neo*menthol with a specific rotation $[\alpha]_D^{18}$ $-19{\cdot}6°$. These optically active *neo*menthols, when oxidised, gave *d*- and *l*-menthones with specific rotations of opposite sign to the *neo*menthol from which they were obtained, so that *d*-menthol and *l-neo*menthol both give *d*-menthone, whilst *l*-menthol and *d-neo*menthol both give *l*-menthone. This relationship bears a striking resemblance to that between the borneols, *iso*borneols, and camphors (compare Pickard and Littlebury, Trans., 1907, **91**, 1973), for example, both *l*-borneol and *d-iso*borneol, when oxidised, give *l*-camphor. As the menthols and *neo*menthols are undoubtedly stereoisomerides, further support is given by analogy to the oft-repeated suggestion that borneol and *iso*borneol are stereoisomerides.

Haller and Martine (*Compt. rend.*, 1905, **40**, 1298) have reduced pulegone by the Sabatier and Senderens method. Two of the menthols obtained by them are obviously more or less impure forms of *l*-menthol and *d-neo*menthol, the latter being named by them "β-pulegomenthol," whilst from Beckmann's researches (*loc. cit.*) it may be concluded that the product to which they give the name α-pulegomenthol belongs to the *iso*menthol series.

It became of interest to determine whether these *neo*menthols could be found in any natural products. By the courtesy of Messrs. Schimmel & Co., who kindly presented the material, the authors have been able to investigate some residues of a "menthol"-like character left, after removal of the *l*-menthol, from a large quantity of Japanese peppermint oil. This product, which had only a small negative specific rotation, was found to contain still some *l*-menthol mixed with some *d*-*neo*menthol. It would appear probable that *l*-menthone is first formed in the plant, and is afterwards reduced to a mixture of *l*-menthol and *d*-*neo*menthol, the *l*-menthol being formed in very much the larger proportion. The reduction of menthone, either optically active or inactive, under laboratory conditions, leads to the formation of menthol and *neo*menthol, but only a very small proportion of the *neo*menthol is obtained under the conditions described in the experimental part.

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* Wallach (*loc. cit.*) from a synthetical specimen of an optically inactive menthone obtained a semicarbazone (m. p. 212°) and an oxime (m. p. 79°). A mixture of menthone and *iso*menthone when treated with semicarbazide in dilute acetic acid solution gives the semicarbazide (m. p. 218°) corresponding with *iso*menthone, whilst the same mixture treated with hydroxylamine gives the oxime (m. p. 80°), which in all probability corresponds with menthone.

EXPERIMENTAL.

Isolation of the Hydrogen Phthalates of Menthol and neo*Menthol from the Thymomenthol of Brunel.*

The crude "thymomenthol" prepared by Brunel's method (*loc. cit.*) by the reduction of thymol was obtained from Messrs. Poulenc Frères, and contained approximately 60 per cent. of "menthols" and 30 per cent. of "menthones," the remainder being unchanged thymol, whilst, as described in the next section, a small quantity (being less than 1 per cent.) of 1-methyl-3-*cyclo*hexanol was isolated from the "menthols."

The thymol was removed from the crude reduction product by repeatedly washing a solution of it in light petroleum with a dilute solution of sodium hydroxide until the last washing gave no milkiness on the addition of dilute hydrochloric acid. The petroleum solution was dried with calcium chloride and distilled. The mixture of "menthones" and "menthols" thus obtained was next heated with a slight excess of phthalic anhydride in an oil-bath kept at 120° for about twelve hours. The product was poured, while still slightly warm, into a large quantity of water containing a slight excess of sodium carbonate, from which, after some time, the "menthones" were extracted with ether.* The hydrogen phthalic esters were precipitated along with some phthalic acid on the addition of hydrochloric acid as a pasty mass, which was then extracted with chloroform, a solvent in which phthalic acid is insoluble. The separation of the pure esters from the crystalline mass remaining after removal of the solvent has been carried out in two ways: (*a*) by the fractional crystallisation of the esters from acetic acid and water, and (*b*) partial precipitation of the magnesium and zinc salts of the hydrogen phthalates, followed by crystallisation of the acid esters from acetic acid.

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* Working with half-kilo. quantities of crude thymomenthol it was found necessary to use about fifteen litres of water to avoid unsatisfactory separation of the ether used in the extraction.

Method (*a*).—The following is a description of the course of one series of crystallisations. The crude esters were crystallised from acetic acid containing about 5 per cent. of water, and the resulting crop of crystals melted (indefinitely) between 135° and 148°. These were repeatedly recrystallised from the smallest possible amount of warm glacial acetic acid, the melting points of the crystals after each successive recrystallisation being 148—158°, 163—167°, 166—169°, 173—176°, 175—177°; thus after six crystallisations a product was obtained with a melting point which was unaltered by further recrystallisation. Systematic fractional crystallisation of successive crops obtained from the first mother liquor by the addition of more water yielded a product which melted at 129—131°, and was unaltered by recrystallisation. This method of isolating the two esters is extremely tedious,* fifty or sixty crystallisations being necessary, whilst the amount of intermediate fractions left at the end of the process is considerable. The amount of the phthalate with the higher melting point, *neo*menthyl hydrogen phthalate, obtained either by this method or by the method (*b*) is about one-fifth of the other ester, menthyl hydrogen phthalate.

Method (*b*).†—This has been applied to the crude mixture of esters, but is more satisfactory if this is previously divided approximately into two portions by one crystallisation from dilute acetic acid. Each portion is then worked up as follows: The ester is dissolved in a cold solution of sodium carbonate, any excess of this being exactly neutralised by hydrochloric acid, and the solution diluted with water, so that the concentration of the ester does not exceed one in forty of the solution. This is then precipitated, first, with a solution of magnesium chloride, and secondly, after removal of the insoluble magnesium salts by filtration, with a solution of zinc chloride.

The magnesium precipitate becomes quite granular after a few hours, is collected, well washed with water, and crystallised three times from 96 per cent. alcohol, after which the pure salt melts and decomposes at 119—122°. It is then redissolved in alcohol, poured into cold dilute hydrochloric acid, and yields the menthyl hydrogen phthalate, which after two crystallisations from acetic acid is pure and melts at 129—131°. On one occasion, when working up a sample of the crude ester which was not completely molten at 150°, a magnesium salt was obtained, which was much more soluble in alcohol than the one just described, melted at 80—82° after two crystallisations from dilute alcohol, and when decomposed by hydrochloric acid gave the pure *neo*menthyl hydrogen phthalate after one crystallisation from glacial acetic acid. The zinc precipitate cannot be crystallised from any of the ordinary media, and is therefore decomposed by shaking with cold dilute hydrochloric acid. The resulting phthalic ester is crystallised twice from glacial acetic acid, when the pure *neo*menthyl hydrogen phthalate melting at 175—177° is obtained. Menthol and *neo*menthol were obtained from the corresponding esters by hydrolysis of these with alcoholic solutions of sodium hydroxide ($2\frac{1}{2}$ mols.). Four or five hours on a boiling-water bath are required for complete hydrolysis. The greater portion of the alcohol was then distilled off on the water-bath, the menthols removed from the residue by a current of steam, and dissolved in ether. The ethereal solution was dried by means of anhydrous magnesium sulphate, and after removal of the ether the menthols were purified by distillation under reduced pressure.

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* The course of separation is probably hindered by the presence of small amounts of esters of one or both of the *iso*menthols, whilst, as previously pointed out, this mixture contains a small amount of the hydrogen phthalates of the methyl*cyclo*hexanol.

† It is essential for success either with method (*a*) or (*b*) that the crude mixture of esters should be entirely free from phthalic acid.

Isolation of 1-*Methyl*-3-cyclo*hexanol from the Crude Thymomenthol.*

The filtrate from the zinc precipitate obtained in method (*b*) described above was acidified with hydrochloric acid, and the small quantity of resulting oil dissolved in ether.* The viscid oil remaining after distilling off the ether became very pasty after remaining in the desiccator for some weeks. It was then crystallised several times from light petroleum, and ultimately obtained in well-defined rods, which melted at 93°.

The same compound was separated by another method. The addition of a solution of calcium chloride to the filtrate from the zinc salts precipitated a calcium salt, which was purified by crystallisation from dilute alcohol, and then gave, when decomposed by hydrochloric acid, the compound melting at 93°. The filtrate from the calcium salt when acidified gave very small amounts of an oil, which after some months slowly crystallised and then melted very indefinitely at about 45°, but has not been identified.†

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* In the course of these experiments several kilos. of crude "thymomenthol" have been worked up. The isolation of these hydrogen phthalates has necessitated the use of solutions of large bulk, from which these small quantities of oil were obtained by filtration through filter paper previously moistened with water.

† It probably contains the hydrogen phthalate of the other isomeride of 1-methyl-3-*cyclo*hexanol. Each of the cresols, when hydrogenated by the Sabatier and

1·4417 Grams of the hydrogen phthalate (m. p. 93°) were neutralised by 0·2220 NaOH; the calculated amount for the hydrogen phthalate of a methyl*cyclo*hexanol is 0·2200 NaOH.

The alcohol obtained after hydrolysis of the compound (m. p. 93°) with an alcoholic solution of sodium hydroxide boiled at 173°/752 mm., and had D_{17}^{17} 0·912. It formed a phenylcarbamate, which crystallised from light petroleum, and melted at 96°. When oxidised with chromic acid, a ketone was produced which gave a semicarbazone melting at 180—181°. These results are identical with some obtained by the authors in working up the products of the hydrogenation of *m*-cresol (compare also Sabatier and Mailhe, *Compt. rend.*, 1905, **140**, 350, and Wallach, *Annalen*, 1896, **289**, 337).

Menthol.

Menthol boils at 103—105°/16 mm., and melts at 34°. It separates from very light petroleum in long, needle-shaped crystals, which have an appearance and odour very similar to those of natural *l*-menthol. It is quite insoluble in water, but readily soluble in the common organic media, and is exceedingly volatile.

Phenylcarbamate.—The phenylcarbamate is formed when molecular proportions of menthol and phenylcarbimide remain for a day at the ordinary temperature. It crystallises from dilute methyl alcohol in small, prismatic needles, and melts at 104°.

Benzoate.—The benzoic ester is prepared by warming a mixture of menthol and benzoic anhydride, and obtained as a viscid oil, which does not solidify at the temperature of a mixture of ice and salt.

Hydrogen Succinate.—Molecular proportions of the menthol and freshly distilled succinic anhydride are heated in an oil-bath at 115—120° for twenty-five hours. The mixture is poured into a solution of sodium carbonate, and extracted with ether to remove unchanged menthol and traces of the dimenthyl succinate. After removing the dissolved ether by blowing a current of air through the solution, it is acidified by the addition of hydrochloric acid, and the hydrogen succinate collected. It crystallises from light petroleum in silky needles, and melts at 85—86° (compare Brunel, *loc. cit.*).

Hydrogen Phthalate.—The hydrogen phthalate was prepared from the menthol in the manner previously described, and after one crystallisation from acetic acid was obtained in stout prisms, which melted at 129—131°:

Senderens method, should give two hexahydro-derivatives. The separation and investigation of these *cis*- and *trans*-isomerides corresponding with the three hydrogenated cresols and other phenols are proceeding in this laboratory.

0·5258 was neutralised by 0·0692 NaOH. Calculated amount required for $C_{10}H_{19}\cdot O\cdot CO\cdot C_6H_4\cdot CO_2H$ is 0·0691 NaOH.

The *magnesium* salt of the hydrogen phthalate crystallises from alcohol in pearly laminæ, and decomposes at 117—118°:

1·4492 gave 0·825 MgO. Mg = 3·41. Calc., Mg = 3·81 per cent.

The *zinc* salt is soluble in water.

neo*Menthol.*

neo*Menthol* boils at the same temperature as its stereoisomeride, and melts at 51°. It is insoluble in water, but is soluble in the common organic media. From light petroleum it crystallises on spontaneous evaporation of the solvent in large, stout, prismatic tablets. It has a pleasant and characteristic odour, which is readily distinguishable from that of menthol or its optically active components.

Phenylcarbamate.—The phenylcarbamate, which is readily formed from the components at the ordinary temperature, crystallises from dilute methyl alcohol in large, prismatic needles, and melts at 114°.

Hydrogen Succinate.—The hydrogen succinate prepared by heating molecular proportions of *neo*menthol and succinic anhydride at 120° for ten hours crystallises from light petroleum, and melts at 67—68°.

Hydrogen Phthalate.—*neo*Menthol was reconverted into the hydrogen phthalate in the manner described above. The product obtained after distilling off the chloroform melted (without any recrystallisation) at 175—177°. It crystallises from warm glacial acetic acid in stout prisms, and is much less soluble in organic media than the corresponding compound of menthol:

0·5712 was neutralised by 0·754 NaOH. Calculated amount required is 0·0751.

The *magnesium* salt, which can be precipitated from concentrated solutions of the sodium salt and magnesium chloride, is somewhat soluble in water, very so in alcohol, and crystallises from a suitable mixture of the two solvents in very slender needles, which contain water of crystallisation, and melt and decompose at 80—82°. After desiccation, they melt (not very sharply) at about 82° and decompose at 135°.

Experiments to Prove the Homogeneous Character of Natural l-*Menthol.*

l-*Menthyl Hydrogen Phthalate.*—This ester was prepared in the manner used in the case of the other phthalates described already. It crystallises from dilute acetic acid in a most characteristic manner, separating out at first as a microcrystalline paste, which melts at about 110°, and on keeping for some days in contact with the mother liquor slowly changes to a number of large, prismatic needles. This stable variety melts at 122° (compare Arth, *Ann. Chim. Phys.*, 1885, [vi], **7**, 487, who gives the melting point as 110°), whilst both varieties have $[\alpha]_D - 91{\cdot}43°$ in 5 per cent. chloroform solution. The *brucine* salt was prepared by dissolving the components in chloroform, and purified after removal of the solvent by crystallisation from dilute methyl alcohol, when it was obtained in small, prismatic needles, which melted and decomposed at 120°, and had $[\alpha]_D - 32{\cdot}62°$ in a 3·5 per cent. solution in anhydrous alcohol. The hydrogen phthalate obtained from the purest brucine salt was hydrolysed by boiling with an alcoholic solution of sodium hydroxide, and gave pure *l*-menthol, which melted at 43°, and when examined in the polarimeter gave the following result:

1·0073, made up to 20 c.c. with anhydrous ethyl alcohol, gave $\alpha - 4{\cdot}98°$ in a 2-dcm. tube, whence $[\alpha]_D - 49{\cdot}44°$.

Another sample of pure *l*-menthol was prepared by the hydrolysis of *l*-menthyl *l*-menthylcarbamate.

l-*Menthyl chlorocarbonate*, $C_{10}H_{19}{\cdot}O{\cdot}COCl$, was obtained by heating in a reflux apparatus for several hours a solution of natural *l*-menthol in benzene with the calculated amount of the additive product of carbonyl chloride and antipyrine (compare D.R.-P. 1901, 117624). The product was filtered from antipyrine hydrochloride, washed repeatedly with water, and dried over calcium chloride. After the benzene had been removed by heating on a water-bath, the residue was fractionally distilled under reduced pressure. *l*-Menthyl chlorocarbonate was thus obtained as a colourless oil with a penetrating odour, boiling at 106—109°/10 mm.

l-*Menthyl* l-*Menthylcarbamate*.—The chlorocarbonate was allowed to react in a reflux apparatus with the calculated amount of *l*-menthylamine dissolved in light petroleum in the presence of an excess of sodium hydrogen carbonate. The reaction mixture was shaken several times with dilute hydrochloric acid to remove any unchanged amine, then with water, and dried over calcium chloride. After distilling off the petroleum, the crude carbamate was purified by recrystallisation from alcohol, from which it was obtained in stout needles melting at 110—111°: 0·5085, made up to 19·95 c.c. with anhydrous ethyl alcohol, gave $\alpha - 4{\cdot}64°$ in a 2-dcm. tube, whence $[\alpha]_D - 91{\cdot}03°$, a value which remained unaltered after further recrystallisation. The carbamate was hydrolysed by boiling with an alcoholic solution of sodium hydroxide ($2\frac{1}{4}$ mols.) in a sealed tube at 140° for ten hours. The *l*-menthol was then removed from the mixture by a current of steam, and further purified by distillation under diminished pressure. It boiled at 104°/9 mm., melted at 43°, and at the same concentration in ethyl alcohol as the other specimen had $[\alpha]_D$ $-49{\cdot}62°$.

From these experiments it may be concluded that pure *l*-menthol has the constants above named, which are the same as those given in the literature.

l-*Menthyl Benzoate.*—The benzoic ester prepared from this pure *l*-menthol melted at 55—56°, and had $[\alpha]_D$ $-84{\cdot}39°$ in a 5 per cent. solution in chloroform and $[\alpha]_D$ $-90{\cdot}59°$ in a 1 per cent. solution in benzene.

l-*Menthyl Hydrogen Succinate.*—This compound, when prepared from the pure *l*-menthol and succinic anhydride in the manner described for the corresponding optically inactive compound, crystallises in long, silky needles, melts at 64°, and has in a 5 per cent. chloroform solution $[\alpha]_D$ $-64{\cdot}00°$ and in a 1·4 per cent. benzene solution $[\alpha]_D$ $-57{\cdot}02°$.

Resolution of Menthyl Hydrogen Phthalate.

d-*Cinchonine* l-*Menthyl Hydrogen Phthalate.*

Cinchonine (1 mol.) readily dissolved in a warm concentrated alcoholic solution of menthyl hydrogen phthalate (1 mol.), and the solution on cooling deposited a crystalline salt. This had a specific rotation in anhydrous ethyl alcohol $[\alpha]_D$ $+60{\cdot}26°$; the melting point was very indefinite; it became pasty at about 63°, and decomposed at 100°. After four recrystallisations from dilute alcohol, the rotatory power was unaltered by further recrystallisation, but the melting point remained indefinite:

1·0645, made up to 20 c.c. with anhydrous ethyl alcohol, gave α $+5{\cdot}67°$, whence $[\alpha]_D$ $+53{\cdot}26°$.

0·2913 gave 12·8 c.c. N_2 (moist) at 22° and 745 mm. $N=4{\cdot}84$.

$C_{37}H_{46}O_5N_2$ requires $N=4{\cdot}68$ per cent.

l-*Brucine* l-*Menthyl Hydrogen Phthalate.*—The mother liquor from the first crystallisation of the cinchonine salt was poured into cold dilute hydrochloric acid, and the resulting hydrogen phthalate recrystallised from acetic acid. The product obtained had a specific rotation in chloroform $[\alpha]_D$ $+12°$, whilst the ester precipitated from the acetic acid mother liquor had $[\alpha]_D$ $+77°$. The phthalic ester with $[\alpha]_D$ $+12°$ was dissolved in chloroform, and one molecular proportion of anhydrous brucine added. The solvent was then distilled off, and the residue kept in the desiccator until it became crystalline, when it was recrystallised nineteen times from the minimum amount of methyl alcohol containing approximately 10 per cent. of water. The brucine salt from the first crystallisation had a specific rotatory power in anhydrous ethyl alcohol $[\alpha]_D$ −10·5°, but as the process went on this became more negative, and ultimately reached the apparently constant value deduced from the following polarimetric result: 0·7009, made up to 20 c.c. with anhydrous ethyl alcohol, gave α −2·09° in a 2-dcm. tube, whence $[\alpha]_D$ −29·82°. The salt, however, was not quite pure, as the specific rotation should have been $[\alpha]_D$ −32·6° (compare p. 118).

l-*Menthyl Hydrogen Phthalate.*—The purest cinchonine salt was dissolved in warm alcohol, and the solution poured into cold dilute hydrochloric acid. The precipitated phthalate was then dissolved in acetic acid, from which it separated in exactly the same way as described above for the corresponding compound prepared from natural *l*-menthol. The large, prismatic needles thus obtained melted at 120—121°: 1·0070, made up to 20 c.c. with chloroform, gave, in a 2-dcm. tube, α −9·04°, whence $[\alpha]_D$ −90·67°; whilst the mother liquor when precipitated with water gave a product which had in a similar solution $[\alpha]_D$ −90·44°.

l-*Menthol.*—The hydrogen phthalic ester thus obtained was hydrolysed by boiling with an alcoholic solution of potassium hydroxide ($2\frac{1}{2}$ mols.) for five hours. Most of the alcohol was then distilled off on the water-bath, and the menthol then removed by a current of steam. It solidified in the distillate, and was pressed out on a porous tile, after which it had $[\alpha]_D$ −48·27°. It was further purified by distillation under diminished pressure, when it melted at 42°:

1·0051, made up to 20 c.c. with anhydrous alcohol, gave, in a 2-dcm. tube, α −4·90°, whence $[\alpha]_D$ −48·76°.

It will be obvious after comparison with the results obtained with natural *l*-menthol that the synthetical product was not yet quite pure, whilst that obtained from the brucine salt described above was even less pure.

The product having $[\alpha]_D$ −48·76° was therefore heated with benzoic anhydride at 120° for twenty hours. The benzoic ester thus obtained boiled at 182—183°/15 mm., and nearly all solidified on cooling. It was pressed out on a porous tile, and recrystallised twice from dilute alcohol. It was then obtained in long needles, which melted at 55—56°:

0·2041, made up to 20 c.c. with benzene, gave, in a 2-dcm. tube, α −1·86°, whence $[\alpha]_D$ −90·65°.

This rotation is the same as that observed for the benzoate of the pure *l*-menthol, and the product obtained by its hydrolysis was identical with the natural product.

d-*Menthol*.—The corresponding *d*-menthol was obtained from the cinchonidine salt of the hydrogen succinic ester of the partly active menthol. The mother liquors containing the most soluble portion of the brucine menthyl hydrogen phthalate were decomposed by pouring into dilute hydrochloric acid, and the resulting hydrogen phthalate was hydrolysed. The strongly dextrorotatory menthol thus obtained was converted into the hydrogen succinic ester by the method previously described. The cinchonidine salt of this ester was prepared by boiling the components in acetone, from which the salt crystallised on cooling in clusters of prismatic needles. After six recrystallisations from acetone the salt melted at 141—143°, had $[\alpha]_D$ $-46{\cdot}72°$ in a 3·5 per cent. solution in ethyl alcohol, and gave a hydrogen succinate, which had $[\alpha]_D$ $+55{\cdot}68°$ in a 1·5 per cent. solution in benzene. It will be observed by comparison with the result quoted on p. 119, that this ester was not quite pure. The *d*-menthol obtained from it by hydrolysis with an alcoholic solution of sodium hydroxide melted at 40°, and in a 3·5 per cent. ethyl alcoholic solution had $[\alpha]_D$ $+48{\cdot}15°$. It was therefore converted into the benzoate, and then after two crystallisations from alcohol yielded the pure d-*menthyl benzoate*, which melted at 56°:

0·1918, made up to 20 c.c. with benzene, gave, in a 2-dcm. tube, α $+1{\cdot}74°$, whence $[\alpha]_D$ $+90{\cdot}72°$.

Resolution of neo*Menthol.*

Brucine d-neo*Menthyl Hydrogen Phthalate*.—*neo*Menthyl hydrogen phthalate (1 mol.) was suspended in warm acetone, and anhydrous brucine (1 mol.) added. After warming for thirty minutes on the water-bath, a clear solution was obtained, which on cooling deposited the crude salt. This commenced to melt at 117°, decomposed at 119°, and in a 5 per cent. alcoholic solution had $[\alpha]_D$ $-8{\cdot}13°$. After six recrystallisations from acetone the specific rotatory power decreased to $[\alpha]_D$ $-1{\cdot}58°$. Further repeated crystallisations from acetone, and also from dilute alcohol, gave successive products, which melted and decomposed at 125—127°, but the rotations * of which varied very irregularly from $[\alpha]_D$ $-2{\cdot}3°$ to $+0{\cdot}4°$. After each crystallisation, therefore, the salt was decomposed, and the resulting hydrogen phthalate examined in the polarimeter. By a very tedious process of selecting the samples of hydrogen phthalate of the highest rotation, the others being reconverted into the brucine salt, which was then recrystallised, it was, however, found possible to isolate a sufficient quantity.

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* The variations were not due to experimental errors, since redeterminations of the rotation of the same sample gave results, the variations of which were very much less than the variations in the rotations of products obtained from successive crystallisations.

d-neo*Menthyl Hydrogen Phthalate.*—The prolonged process * just described did not furnish the dextrorotatory hydrogen phthalate in quite a pure condition. The product of highest rotation was crystallised from acetic acid, then melted at 142—144°, and had, in a 2·5 per cent. solution in chloroform, $[\alpha]_D + 68\cdot71^\circ$, whilst the addition of water to the mother liquor gave a product which had the same melting point, but a rotatory power $[\alpha]_D + 69\cdot28^\circ$. A similar result was obtained when these two products were mixed and recrystallised from benzene, the first crop of crystals having $[\alpha]_D + 67\cdot53^\circ$ when dissolved in chloroform. It was therefore evident that this specimen of the phthalate with $[\alpha]_D + 68\cdot71^\circ$ was not quite pure. As, however, the derivatives of optically inactive *neo*menthol are in general far less soluble than the corresponding optically active compounds, attempts at further purification were abandoned, and this hydrogen phthalate was hydrolysed in the manner described for similar compounds.

The *d-neo*menthol thus obtained boiled at 98°/16 mm., did not solidify at the temperature of a mixture of ice and salt, had a density approximately 0·90, and gave α_D^{18} $+4\cdot43^\circ$ in a 25 mm. tube, whence $[\alpha]_D + 19\cdot69^\circ$. Its odour was quite distinct from that of *d*- or *l*-menthol. It formed an oily benzoate, and when reconverted into the hydrogen phthalate yielded a product which, after crystallisation from acetic acid, had $[\alpha]_D + 62\cdot66^\circ$ when dissolved in chloroform. A further quantity of this *d-neo*menthol was prepared by the hydrolysis of various specimens of the hydrogen phthalate, which had respectively $[\alpha]_D + 67\cdot45^\circ$, $+ 68\cdot21^\circ$, $+ 61\cdot4^\circ$, $+ 65\cdot49^\circ$, $+ 66\cdot58^\circ$, $+ 62\cdot66^\circ$; it gave $\alpha + 4\cdot35^\circ$ in a 25 mm tube, and was used for the preparation of *l*-menthone (see p. 124).

l-neo*Menthol.*—The first mother liquor from the crystallisation of the brucine salt of the *neo*menthyl hydrogen phthalate was poured into excess of dilute hydrochloric acid, and the precipitated ester washed well and dried on a porous tile. It then melted at about 165°, and had $[\alpha]_D - 32^\circ$ in a 5 per cent. solution in chloroform. Attempts to obtain a product with a higher negative rotation by the recrystallisation of the cinchonidine or quinine salts were unsuccessful. The hydrogen phthalic ester was therefore hydrolysed in the usual way, and the feebly lævorotatory *neo*menthol converted in the hydrogen succinic ester, which then had $[\alpha]_D - 14^\circ$ in a 5 per cent. solution in chloroform. The cinchonidine salt of this hydrogen succinate decomposed when warmed with solvents, but the *quinine* salt was found to crystallise readily from warm acetone. This salt at first melted at 133—135°, and in a 5 per cent. alcoholic solution had $[\alpha]_D -113\cdot5^\circ$. After six recrystallisations the salt was obtained as a felted mass of beautiful, silky needles; it then melted at 139—142°, and had $[\alpha]_D -120\cdot8^\circ$, a value which was unaltered by further recrystallisation. l-neo*Menthyl hydrogen succinate* was then obtained by decomposing a warm alcoholic solution of the salt with cold dilute hydrochloric acid. The crude ester had $[\alpha]_D -33\cdot91^\circ$ in a 5 per cent. chloroform solution, but probably contained a little quinine hydrochloride. When crystallised from light petroleum it was obtained in very large, glassy, flat prisms, which melted at 68° and had $[\alpha]_D -33\cdot04^\circ$. The second crop of crystals had a slightly higher rotatory power, namely, $[\alpha]_D -33\cdot35^\circ$, so that the product was probably not quite pure.

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* It was found impossible to crystallise any salt prepared from the numerous other alkaloids tried.

l-neo*Menthol*, obtained by the hydrolysis of the succinic ester with an alcoholic solution of sodium hydroxide, was a colourless oil of pronounced odour, similar, but quite distinct from *l*-menthol. It boiled at 105°/21 mm., and did not solidify when kept at −15°. It had n_D^{20} 1·46031,* D_4^0 0·9124, D_4^{20} 0·8995, and D_4^{30} 0·8917. When examined in a 50 mm. tube in the polarimeter, it gave $\alpha^{4\cdot5} -8\cdot90^\circ$, $\alpha^{18} -8\cdot87^\circ$, and $\alpha^{29\cdot5} -8\cdot79^\circ$, whence $[\alpha]_D^{4\cdot5} -19\cdot57^\circ$, $[\alpha]_D^{18} -19\cdot62^\circ$, and $[\alpha]_D^{29\cdot5} -19\cdot72^\circ$.

Phenylcarbamate.—The phenylcarbamate was readily formed when molecular proportions of the *neo*menthol and phenylcarbimide were allowed to remain for one day. It crystallised from dilute methyl alcohol in slender needles, melted at 107—108°, and in a 5 per cent. solution in chloroform had $[\alpha]_D -26\cdot77^\circ$.

The Menthones obtained by the Oxidation of Menthol, neo*Menthol, and their Optically Active Components.*

The menthols now described have been oxidised to the corresponding menthones by means of a chromic acid mixture, the procedure of Beckmann (*loc. cit.*) being closely followed. Beckmann used the method for the oxidation of natural *l*-menthol, and the characteristic phenomenon of the process is the formation of a microcrystalline, black chromium compound of *l*-menthol, which suddenly decomposes when the temperature is raised to about 53°, with the separation of *l*-menthone. The oxidation of *r*-menthol proceeded in a similar manner, but the chromium compound did not decompose until about 65°, whilst in the case of the *neo*menthols the oxidation was found to take place just below 50°. It was found preferable to dry the ethereal solutions of the menthones with anhydrous magnesium sulphate instead of sodium sulphate. It was necessary to adhere very strictly to the directions given by Beckmann owing to the readiness with which the menthones undergo "inversion."

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* The authors are indebted to Dr. T. M. Lowry for the determination of the refractive index of *l*-*neo*menthol.

r-Menthol oxidised in this manner gave a 90 per cent. yield of optically inactive *menthone*, which was obtained as a colourless oil with a strong odour of peppermint, and boiling at 205°/748 mm. The *oxime* was precipitated by water from an alcoholic solution of menthone and hydroxylamine which had remained for twelve hours; it was crystallised twice from alcohol, and was obtained in feathery needles, which melted at 80° (compare Brunel, *loc. cit.*). The *semicarbazone* was prepared by mixing alcoholic solutions of menthone and semicarbazide acetate; after two crystallisations from alcohol it was obtained in small nodules, which melted at 158°.

*r-neo*Menthol was oxidised in the same manner. The menthone obtained boiled at 204°/735 mm., and formed quantitatively an oxime and semicarbazone. These derivatives had the same melting points as the respective compounds prepared from the menthone obtained by the oxidation of *r*-menthol, and were further shown to be identical with these by the "mixed melting-point" method.

l-Menthol has been oxidised by many investigators, and the resulting *l*-menthone has been described as having various rotatory powers from $[\alpha]_D$ −24·78° to $[\alpha]_D$ −28·18°. Taking every care to exclude traces of alkali and oxidising pure *l*-menthol, it was found that the *l*-menthone of maximum rotatory power obtainable had $[\alpha]^{19}_D$ −29·10° and D^{19}_4 0·896. The semicarbazone of this menthone melted at 189°.

The oxidation of the slightly impure specimen of *d-neo*menthol mentioned on p. 122 gave a sample of *l*-menthone, which boiled at 204°/750 mm., and had $[\alpha]^{19}_D$ −23·3°. The semicarbazone of this ketone after one recrystallisation from alcohol melted at 187°.

The purest *l-neo*menthol obtained was oxidised, and gave d-*menthone*, which boiled at 204°/750 mm., and had D^{18}_{18} 0·895. In a 50 mm. tube it had α^{18} +11·12°, whence $[\alpha]^{18°}_D$ +24·85°. The *semicarbazone* prepared from this *d*-menthone melted at 187—189°. Equal amounts of this semicarbazone and that prepared from the *l*-menthone obtained by the oxidation of *d-neo*menthol were carefully mixed, when it was found that the product melted at 159—160°, and did not depress the melting point of *r*-menthonesemicarbazone.

Reduction of the Menthones.

r-Menthone was reduced by means of hydrogen in the presence of finely divided nickel heated to 180°. The resulting product was heated with phthalic anhydride, and the hydrogen phthalates were worked up in the manner previously described. The hydrogen phthalate obtained by decomposition of the recrystallised magnesium salt melted at 129°, and when mixed with *r*-menthyl hydrogen phthalate melted at the same temperature. The ester obtained from the zinc salt melted at 166—170°, and was recrystallised once from glacial acetic acid, when it melted at 175—177°, and mixed with *r-neo*menthyl hydrogen phthalate melted at the same temperature. Similar results were obtained by the more tedious process of fractional crystallisation of the hydrogen phthalates from acetic acids, and no indications were observed of the presence of other hydrogen phthalates.

The unreduced ketone which had been extracted by ether from the solution of the hydrogen phthalates in sodium carbonate was purified in the usual manner, and 15·4 grams of it were treated with semicarbazide acetate in alcoholic solution. The melting points and weights of successive crops were: (*a*) 149—156°, 11·5 grams; (*b*) 150—180°, 3·4 grams; (*c*) 180—195°, 3·9 grams; and (*d*) precipitated by the addition of water, 170—190°, 1·2 grams; that is in all 20 grams, the calculated amount being 21·1 grams. The semicarbazone (m. p. 180—195°) was recrystallised from alcohol, in which it was very sparingly soluble, when a product was obtained which melted at 217°. The formation of the semicarbazone was attributed to the probable "inversion" of the menthone to *iso*menthone by the heating with phthalic anhydride. This view was supported by an experiment in which pure *l*-menthone, $[\alpha]_D -29°$, was heated at 120° for some hours with phthalic anhydride, when the rotatory power was inverted to $[\alpha]_D +13°$.

r-Menthone was also reduced in moist ether with finely divided sodium. The product was almost pure *r*-menthol, as it solidified almost completely, and after draining on a porous tile melted at 34°.

In another experiment *r*-menthone was reduced by sodium in a mixture of ether and alcohol. From the product a large amount of *r*-menthyl hydrogen phthalate (m. p. 129—131°) was isolated, and also by means of the "magnesium-zinc salt" treatment a small amount of *neo*menthyl hydrogen phthalate, whilst there was some indication that small amounts of other menthols were present (compare Beckmann, *loc. cit.*).

l-Menthone was reduced by the Sabatier and Senderens process, and the resulting mixture of menthols converted into hydrogen phthalic esters. These esters were separated by precipitation of the magnesium and zinc salts into (i) the magnesium salt of *l*-menthyl hydrogen phthalate, which melted at 119—121°, and gave the corresponding hydrogen phthalate (m. p. 121° and $[\alpha]_D -91·10°$ in chloroform solution), and (ii) about one-fifth as much impure *d-neo*menthyl hydrogen phthalate, which melted at 138—141°, and had $[\alpha]_D$ $+24 \cdot 25°$ in chloroform solution.

Proof that Japanese Peppermint Oil contains d-neo*Menthol.*

The authors were presented by Messrs. Schimmel & Co. with some material which had been obtained by them from Japanese peppermint oil in the following manner: "Das von dem gewöhnlichen Menthol möglichst befreite Oel wurde nach Wegnahme des Vor- und Nachlaufs mit der gleichen Menge Benzoylchlorid erwärmt. Nach Aufhören der Salzsäureentwickelung wurde es mit Soda gewaschen und darauf Wasserdampf eingeleitet. Es gingen Menthon und andere leicht flüchtige Substanzen über, während die Benzoylverbindung der Menthole zurückblieb. Diese wurde verseift und das erhaltene Menthol destillirt. Hierbei wurde ein flüssiger Vorlauf erhalten, der mit Kolonne fünfmal fracktionirt wurde. Das Endprodukt hatte folgende Eigenschaften: Siedepunkt 80—82°/4 mm., D^{15} 0·9032, α_D $-8°48'$, Mentholgehalt ca. 90 per cent."

This product was converted into hydrogen phthalic esters, and then subjected to a systematic fractional crystallisation from acetic acid. The first crop of crystals melted at 140—143°, and had a rotatory power in chloroform $[\alpha]_D$ $+4 \cdot 58°$. After twenty-eight recrystallisations from the minimum amount of acetic acid containing 5 per cent. of water, a hydrogen phthalic ester was obtained, which melted at 141—144°, and had $[\alpha]_D$ $+57 \cdot 16°$ in chloroform. That this substance was almost pure *d-neo*menthyl hydrogen phthalate, still, however, containing a little *l*-menthyl hydrogen phthalate, is shown by the following experiments: (i) an intimate mixture of equal amounts of it and *d-neo*menthyl hydrogen phthalate melted at 142—144°, whilst a similar mixture (made in chloroform solution) of accurately weighed amounts of it and *l-neo*menthyl hydrogen phthalate melted (without any recrystallisation) at 173—175°; (ii) the ester was hydrolysed, and the resulting alcohol oxidised, when almost pure *l*-menthone was obtained, it having $[\alpha]_D$ $-28 \cdot 33°$, and forming a semicarbazone, which melted at 187—189°.

The first mother liquor left from the crystallisation of the crude hydrogen phthalates was carefully worked up, and from it was obtained pure *l*-menthol. These results were afterwards confirmed by the oxidation of a mixture of menthols obtained from specimens of the esters, of which the rotatory powers varied from $[\alpha]_D$ $-5°$ to $[\alpha]_D$ $+40°$. This mixture of menthols had $[\alpha]_D$ $+0 \cdot 46°$, and when oxidised gave nearly pure *l*-menthone, which had $[\alpha]_D$ $-27 \cdot 5°$, and formed a semicarbazone melting at 187—189°.

The authors wish to thank Messrs. Schimmel & Co. for their kind gift of material, and also the Research Fund Committee of the Society for a grant which has defrayed some of the cost of this investigation.

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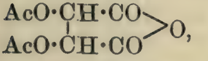
XIII.—*The Conductivity and Dissociation of Diacetyltartaric Acid.*

By Stella Deakin and Albert Cherbury David Rivett.

It has recently been pointed out (Rivett and Sidgwick, Trans., 1910, **97**, 1685) that some connexion may possibly exist between the first dissociation constant of a dibasic organic acid and the rate at which its cyclic anhydride combines with water, the greater the constant the more rapid being the hydration. An attempt to measure the rate of hydration of diacetyltartaric anhydride,  $\left.\begin{array}{l}\mathrm{AcO{\cdot}CH{\cdot}CO}\\ \quad\ |\\ \mathrm{AcO{\cdot}CH{\cdot}CO}\end{array}\right>\mathrm{O}$, at 25° showed it to be too great for determination by the method hitherto adopted (*loc. cit.*, pp. 732 and 1677). It was therefore of interest to obtain a measure of the dissociation constant of the acid. Some figures by Walden (*Zeitsch. physikal. Chem.*, 1891, **8**, 473) are available, but it is impossible to deduce a constant from them, since at the dilutions measured, between 32 and 1024, the second dissociation is already too considerable to be neglected.

The anhydride is formed when tartaric acid and acetyl chloride are heated together for several hours. The acid slowly dissolves, and on cooling a solid mass of anhydride and acetic acid is formed, from which the latter may be pressed out or volatilised, and pure anhydride obtained in very long, prismatic crystals by sublimation in a current of carbon dioxide. The crystals are deliquescent in air, and melt at 128—129°. The preparation has been described by Pilz (*Jahresber.*, 1861, 368), Perkin (*Annalen, Suppl.*, 1867, **5**, 287), and Anschütz and Pictet (*Jahresber.*, 1882, 856); the melting points given by these authors are 135°, 126—127°, and 125—129° respectively. Solutions of the acid were made directly from the anhydride.

In table I are given the results of conductivity measurements of comparatively strong solutions. The cell used was a simple form with the electrodes attached to glass tubes passing through a ground cap, which fitted externally to the neck of a flask about

30 c.c. in volume. It was standardised with potassium chloride 0·01- and 0·1-N; the conductivity of the water used in making up solutions was between 0·8 and 1·0 × 10^{-6} mho. A few measurements of density and fairly approximate viscosity (water at 25° = 1) are added, made respectively in a 25 c.c. pyknometer with side capillary, and a single Ostwald viscometer of one hundred and forty seconds' flow with water.

TABLE I.

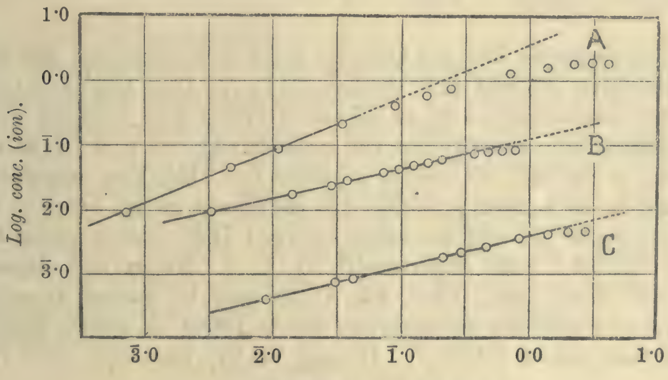
M.	Specific conductivity.	$K_1(2)$.	$K_1(\eta)$.	$K_1(2·125)$.
0·8586	0·03215	0·95	2·37	(0·70)
0·6891	0·03172	1·13	2·52	(0·87)
0·5530	0·03041	1·33	2·68	(1·02)
0·4434	0·02847	1·57	2·63	(1·14)
0·2669	0·02330	1·80	2·65	1·33
0·2141	0·02090	1·96	2·57	1·37
0·1715	0·01866	2·04	2·57	1·40
0·1376	0·01651	2·07	2·52	1·40
0·1100	0·01453	2·11	2·45	1·40
0·0661	0·01070	2·17	2·37	1·39
0·0530	0·00929	2·18	2·36	1·37
0·03182	0·00665	2·23	2·37	1·35
0·01274	0·00354	2·70	2·80	1·51

M.	Density (water = 1).
0·8586	1·0615
0·4434	1·0322
0·1376	1·0100
0·00668	1·0006

M.	Viscosity (water = 1).
0·5531	1·345
0·2141	1·121
0·0661	1·034

M gives molar concentrations per litre. The values of the fraction $C^2_{\text{ion}}/C_{\text{mol.}} \times 10^{-2}$ are given under $K_1(2)$, assuming the degree of dissociation to be μ/μ_∞ (using customary symbols), and the acid to be monobasic, that is, to give only the ions H˙ and HX'. The respective mobilities of these ions have been taken as 347 and 28. There is a steady increase in the values of $K_1(2)$ throughout. If a correction of the molecular conductivity for viscosity is introduced on the assumption of an inverse linear proportionality, by taking the degree of dissociation to be $\mu\eta/\mu_\infty$, where η is the viscosity relatively to water at 25°, the figures in the column $K_1(\eta)$ are obtained. Here the agreement is good in all but the weakest solution, the case being the same as that of acetic acid (Rivett and Sidgwick, *loc. cit.*, p. 736). In this latter case, values for $K_1(2)$ in weak solutions become identical with those of $K_1(\eta)$ at so high a concentration as 0·9. In the case of diacetyltartaric acid, the second dissociation puts measurements in dilute solution out of court, but it is reasonable to suppose that the figure obtained on the assumed viscosity relation, namely, 2·5 × 10^{-2}, represents to a close approximation the first dissociation constant. The comparable value for maleic acid is 1·21 × 10^{-2}, or about half as great. Since the rate of hydration of maleic anhydride, which contains the same five-atom ring as diacetyltartaric, was found to be almost at the limit of possible measurement, it reasonably follows that if the view of a dependence between dissociation constant and rate of hydration be correct, the rate for diacetyltartaric anhydride should be too great for measurement at 25°, as has been found to be the case.

If $\log C_{\text{ion}}$ is plotted against $\log C_{\text{mol.}}$, the curve B shown in the adjoining figure is obtained. It is of the same type as that which Bancroft (*Zeitsch. physikal. Chem.*, 1899, **31**, 191) has shown to be typical for certain salts, acids, and bases. The straight line extends to a concentration about 0·3 molar, and the slope (abscissa against ordinate) is 2·125. Putting this number as the index of $C_{\text{ion.}}$ in the dilution formula, the figures in the last column of table I are



Log. conc. (*mol.*).

A. Hydrochloric acid. *B. Diacetyltartaric acid.*
C. Acetic acid.

obtained. The agreement about a mean value $1·37 \times 10^{-2}$ is good up to the concentration cited, the most dilute solution excepted. In no case of a highly dissociated electrolyte did Bancroft find the index so high as 2. It varies between 1·35 and 1·55. For comparison the curve for hydrochloric acid (measurements at 25° by Masson, quoted in other units by Green, Trans., 1908, **93**, 2040) is shown in the diagram (A). The slope of the straight portion is about 1·5. Although highly dissociated as compared with other organic acids of its class, diacetyltartaric is a weak acid as compared with a halogen hydride, and it may be expected to come under the limiting case of Ostwald where the index = 2. This case is well illustrated by acetic acid, the curve for which (C in figure) has a slope 2·02. The fact that the value in the case of diacetyltartaric acid is greater than 2, points to C_{ion} being greater than is to be expected, and suggests that the second dissociation is appreciable even in these stronger solutions. To obtain an idea of the magnitude of the second constant is not easy, since addition of alkali to form the acid salt may possibly cause some hydrolysis of the acetyl groups, but a rough idea of its value is obtainable, on certain assumptions, from the conductivity measurements of dilute solutions, quoted in table II.

Table II.

M.	Specific conductivity.	$K_2 \times 10^2$.	*M.*	Specific conductivity.	$K_2 \times 10^2$.
0·00668	0·002383	—	0·000942	0·000506	0·103
0·00379	0·001548	0·041	0·000919	0·000498	0·106
0·002843	0·001241	0·067	0·000691	0·000394	0·115
0·002132	0·000991	0·084	0·000346	0·000215	0·110
0·001674	0·000809	0·088	0·000176	0·000115	0·087
0·001257	0·000641	0·096			

The assumptions are (1) that at these concentrations the first dissociation to $H^{\cdot}$ and HX' is complete; (2) that the ions move with the same velocities as at infinite dilution (the viscosity effect being negligible); and (3) that the conductivity due to X'' is double that due to the HX' ion which produces it. This third assumption will hold if, as is most probable, the difference in size between the doubly-charged X'' and the singly-charged HX' ions is negligible. In support of it, the experiments of A. A. Noyes and Stewart (*J. Amer. Chem. Soc.*, 1910, **32**, 1142) may be quoted, in which it was shown that the conductivity due to $(SO_4)''$ is almost exactly double that due to $(HSO_4)'$. It may readily be shown now that

$$\frac{C_{H^{\cdot}} \times C_{X''}}{C_{HX'}} = \frac{M\alpha(1+\alpha)}{(1-\alpha)},$$

where α is the fraction of HX' ionised to $H^{\cdot}$ and X''. Under K_2 are given the values obtained for this expression, multiplied by 100. No approach to constancy is obtained in concentrations above 0·0015 (molar), but below this the values approximate to $0{\cdot}11 \times 10^{-2}$, which, if the above not unobjectionable assumptions hold, gives the order of the second dissociation constant.

Any vitiation of the measurements owing to hydrolysis of the acetyl groups is slight, for such action certainly proceeds slowly, and it is interesting to add that the conductivity of a solution very slowly decreases on keeping. If this is due, as it is reasonable to suppose, to a slow hydrolysis, it follows that one molecule of the relatively strong diacetyltartaric acid gives more hydrogen ion than one of the weaker tartaric and two of acetic acids in presence of one another formed from it.

In the weaker series, no one solution was used for more than four measurements, but in the stronger the whole series was done by the method of dilution, checked by direct titration, from the single original strong solution.

The authors wish to acknowledge their indebtedness to the kindly criticism of Professor Orme Masson.

UNIVERSITY OF MELBOURNE.

XIV.—*The Decomposition of Nitric Acid by Light.*

By WILLIAM COLEBROOK REYNOLDS and WILLIAM HENRY TAYLOR.

ALTHOUGH the decomposition of nitric acid by light has been familiar to chemists for a very long time, the nature and conditions of the reaction do not appear to have been closely examined until 1898, when Berthelot (*Compt. rend.*, 1898, **127**, 143) investigated this among several other photochemical reactions. Berthelot showed that the products of the decomposition of the acid under the influence of light are oxygen, nitrogen peroxide, and water, and that the same products are obtained when the anhydrous acid is heated in exhausted tubes to 100° in the dark for some hours. The decomposition might, therefore, be represented by the equation:

$$4HNO_3 = 2H_2O + 2N_2O_4 + O_2,$$

and Berthelot stated that the reaction was not reversible.

Berthelot dealt with the action of light on nitric acid without differentiating between its influence on the vapour and liquid respectively, and was thus probably unaware of the interesting observation which Veley and Manley (*Phil. Trans.*, 1898, **191**, 365) had made a few months earlier, that light appeared to act only on the vapour of the acid, and not on the liquid.

In the course of attempts to prepare specially pure nitric acid by distillation in a vacuum over various materials, the present authors were led to suspect that appreciable decomposition of the distillate occurred through the action of weak diffused daylight.

Examination of this point resulted in several other phenomena connected with the action of light on nitric acid being investigated, and the results obtained may be briefly summarised at the outset as follows:

(1) Veley and Manley's observation that light acts only on the vapour of nitric acid, and not on the liquid, is fairly conclusively confirmed, and a number of further conditions affecting the

decomposition of nitric acid of different strengths have been investigated.

(2) The reaction is reversible, the products of the decomposition of nitric acid by light re-combining in the dark.

(3) Anhydrous nitric acid (100 per cent.) decomposes spontaneously in the dark.

Conditions Affecting the Decomposition of Nitric Acid by Light.

When a glass tube partly filled with nitric acid is exhausted, sealed, and exposed to light, the decomposition may be followed qualitatively by the colour, intensified if necessary by the subsequent addition of various reagents, and quantitatively by the pressure of the oxygen or titration of the nitrogen peroxide by permanganate solution. When long exhausted tubes partly filled with nitric acid of concentrations up to 100 per cent., having the vapour space carefully screened from light by several folds of black silk bandages, were exposed to direct sunlight for several days, the liquid remained colourless, showing that little or no formation of nitrogen peroxide had occurred; subsequent exposure of the vapour to direct sunlight for one minute caused an appreciable amount of decomposition, as was evident from the colour of the vapour. These results, therefore, confirm Veley and Manley's observation that light acts only on the vapour. If a little carbamide is previously dissolved in the acid, the decomposition proceeds in the vapour as before, and oxygen accumulates in the vapour space, but the peroxide is absorbed and decomposed, and the liquid remains colourless.

The bright yellow colour of the solution of nitrogen peroxide in nitric acid renders the decomposition very evident when the strength of the acid is more than 65 per cent. At greater dilutions it becomes less noticeable and smaller in amount. Berthelot states that decomposition does not occur with 60 per cent. acid. Careful comparisons have shown, however, that the colour can be observed with 50 per cent. acid in strong sunlight, and if either *m*-phenylenediamine or potassium iodide is subsequently added to the exposed sample, evidence of decomposition can still be observed, even with acid of 10 per cent. strength.

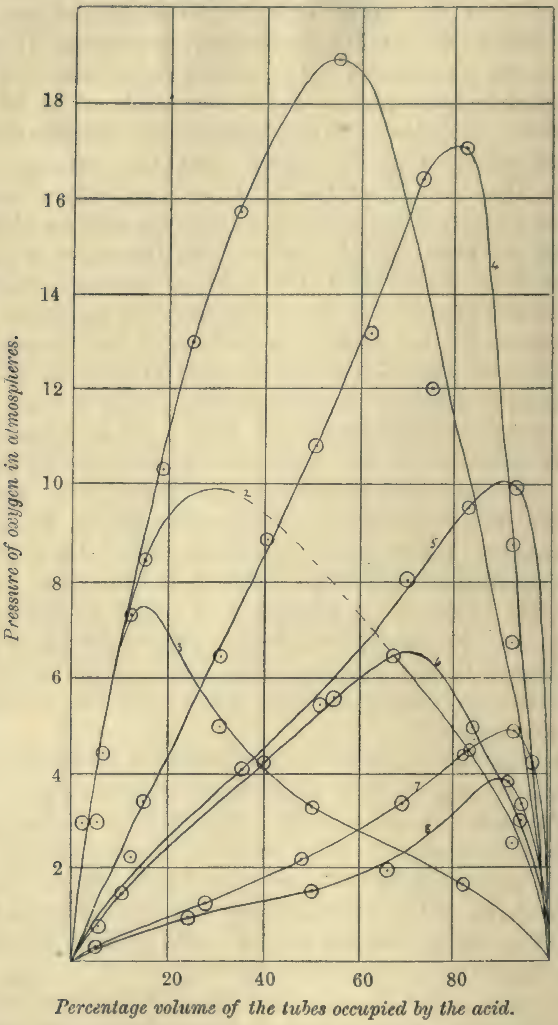
If a number of glass tubes are filled to different extents with nitric acid, and then exhausted, sealed, and exposed side by side to direct sunlight, the pressures in the tubes are very different. Under suitable conditions considerable pressures have been obtained, and it is possible to reach pressures of over eighteen atmospheres, as will be seen in Fig. 1, even in sunlight in the neighbourhood of London. These results form a striking contrast to those obtained by Berthelot, for in only one instance did he observe a pressure greater than one atmosphere. For any given strength of acid and intensity of the light, the maximum pressure is produced when the liquid occupies a certain proportion of the volume of the tube. In the accompanying diagram (Fig. 1) this has been shown graphically. The ordinates indicate the pressure of the oxygen in atmospheres at 18° over acids of 70, 80, 90, and 100 per cent. strengths, and the abscissæ the percentage volume of the tube occupied by the liquid. As the pressure observed depends on the intensity of the light, in comparative experiments for plotting a curve the exposures were made side by side for the same length of time. With weaker light the curve is similar in shape, but falls within that for light of greater intensity, but although in the case of the anhydrous acid the maximum pressure is reached when a much smaller proportion of the tube is occupied than is the case when 70 per cent. acid is present, it will be noticed that the positions of the maxima in Fig. 1 vary with the month in which the exposures were made. This is due partly to the greater intensity of the light during the summer months as compared with the spring months, and partly to the fact that in the summer, the days being longer than in the spring, the light acts for a longer time, inducing decomposition, whilst the nights being shorter recombination (which is referred to later) has less opportunity to take place. If it were possible to get brilliant sunshine continuously all the twenty-four hours, the proportion of the acid corresponding with the maxima might conceivably be nearly the same for different dilutions, namely, when the tube is rather more than nine-tenths filled.

Nitric acid sealed in vessels of very different shape and size and exposed side by side to light gives the same pressures if the acid occupies the same relative volume. The duration of the exposures before the decomposition ceases varies considerably. A tube of 70 per cent. acid one-sixth occupied takes about three to four hours in bright sunlight, but if five-sixths full will require ten to fourteen days. With stronger acid the time is much greater, 100 per cent. acid requiring twice as long an exposure.

Ordinary glass tubes were used in the experiments, but a comparison of glass and clear quartz tubes under similar conditions showed that the pressure was greater in the latter in the ratio of 7:10. Blue and colourless glass tubes gave identical results, but only slight decomposition occurred in an amber-coloured tube.

FIG. 1.

Decomposition of nitric acid.



1. 100 per cent. acid exposed 30 days in August and September, 1910.
2. 100 ,, ,, 25 ,, May, 1910.
3. 100 ,, ,, 20 ,, March, 1910.
4. 90 ,, ,, 30 ,, August and September, 1910.
5. 80 ,, ,, 28 ,, May, 1910.
6. 80 ,, ,, 15 ,, March, 1910.
7. 70 ,, ,, 25 ,, May, 1910.
8. 70 ,, ,, 21 ,, February, 1910.

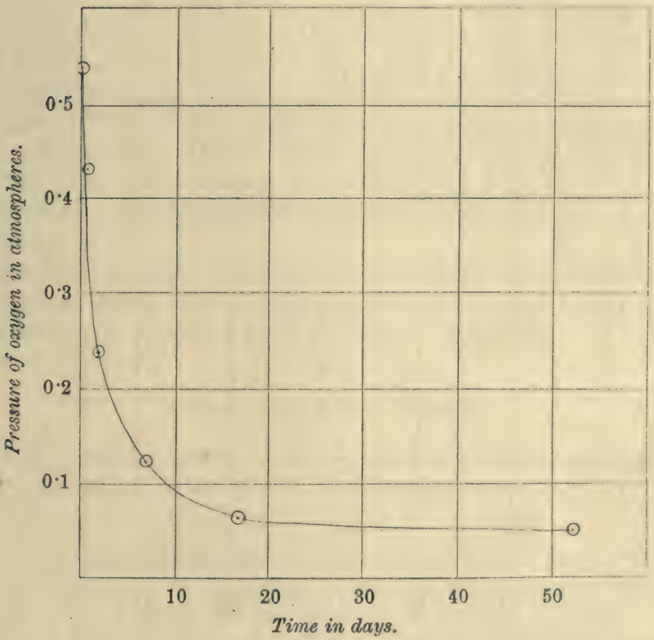
Recombination of the Decomposition Products in the Absence of Light.

Berthelot states that the decomposition is not reversible. Further investigations have shown that he was mistaken, having been misled by the slowness of the change in the reverse direction with concentrated acid, and the fact that he was not aware of the influence of the space relationships referred to above.

When a number of similar tubes of 70 per cent. acid filled to the same extent are fully exposed and then kept in a dark place, the pressure is found to have become halved in thirty-six hours, and after several weeks the acid is only slightly coloured and nearly all the oxygen absorbed.

FIG. 2.

Recombination of 70 *per cent. acid in the dark.*



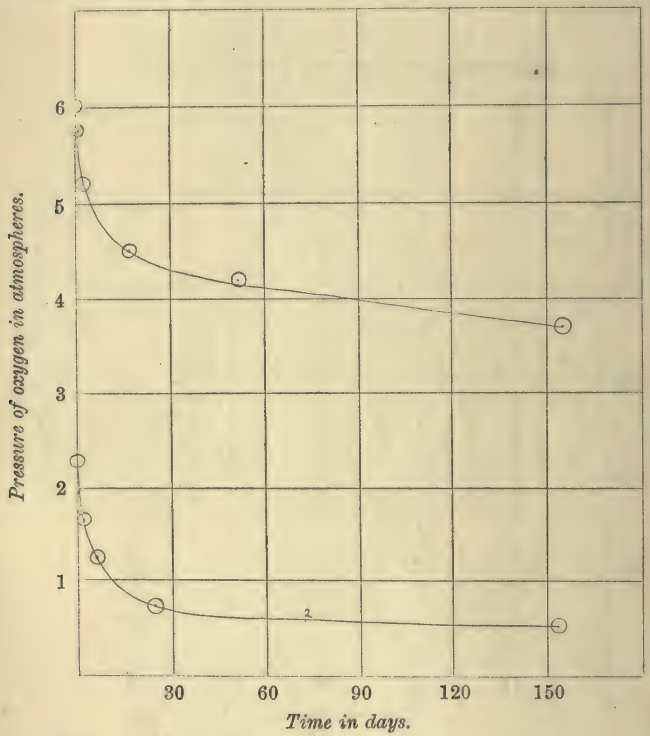
In the case of 85 per cent. acid a similar effect was observed, but the rate of recombination, like that of decomposition, is slower.

When 85 per cent. acid was decomposed in a sealed tube at 240°, the cooled product recombined at a similar rate during several weeks.

When, however, 100 per cent. acid was examined, a somewhat different behaviour was noticed; recombination slowly occurred, but even after many weeks the pressure was still more than half of the original, and no further appreciable diminution was observed. The rate of recombination is shown in the accompanying curves, Figs. 2 and 3. In the last case it will be seen that about half the possible recombination is indicated as probable.

FIG. 3.

Recombination of: 1. 100 *per cent.;* 2. 85 *per cent. acid in the dark.*



Spontaneous Decomposition of 100 *per cent. Nitric Acid in the Dark.*

Samples of 70 and 90 per cent. acids stored in sealed and exhausted tubes in the dark remained colourless after many weeks. Acid of 100 per cent. remained colourless for a few weeks, but after the lapse of twelve months was found to be bright yellow and under a pressure of 9·7 atmospheres (the acid occupied 78 per cent. of the tube).

On repeating the observation with a fresh sample, it again remained colourless for a month, but shortly afterwards commenced to decompose.

A third and fourth series confirmed the results. The pure acid at the ordinary temperature appears to undergo an "induction period" of about a month, during which no noticeable change occurs in the dark; decomposition subsequently occurs, and slowly proceeds, presumably, after many months, reaching the equilibrium, obtained in the reverse of the decomposition by light, when the same proportion of the space is occupied by the acid.

The great difference in behaviour between the anhydrous acid and concentrated aqueous solutions may be due to the presence of a trace of nitrogen pentoxide in equilibrium with the former. Saposchnikoff (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 518; compare Veley and Manley, *Proc. Roy. Soc.*, 1901, **69**, 86; *Phil. Mag.*, 1902, [vi], **3**, 118; and Trans., 1903, **83**, 1015) has shown that a measurable amount of the latter is present in the vapour over mixtures of nitric and sulphuric acids, when the sulphuric acid exceeds a certain proportion. On the other hand, mixtures of equal volumes of pure nitric and sulphuric acids have been kept for nine months in the dark. They remained quite colourless, and no oxygen was liberated.

The high pressure resulting on storing the anhydrous acid in air-tight containers for lengthy periods deserves consideration from those engaged in handling it; it may conceivably have been the cause of accidents.

Discussion of the Results.

The simplest expression in one equation for the changes produced by the action of light on nitric acid is:

$$4HNO_3 \rightleftharpoons 2H_2O + 2N_2O_4 + O_2,$$

but the decomposition may possibly take place in stages, the first product being nitrous acid and oxygen, the former and the excess of nitric acid then producing water and nitrogen peroxide.

As a problem in heterogenous equilibrium, the decomposition of nitric acid by light may perhaps be compared to cases of dissociation by heat, but is complicated by several causes. Assuming that both decomposition and recombination take place in the vapour space, according to the above equation the pressure of the oxygen should vary inversely as the square of the concentration of both the water and the peroxide present in the vapour. For a given strength of acid the concentration of the water and the acid in the vapour space may be regarded as constant when more than a small proportion of acid is present. A rapid rise in the pressure of the oxygen, with increasing concentration of the acid, was therefore to be expected. Most of the peroxide dissolves in the acid. If the proportion of this latter is small, it forms a deep yellowish-brown solution; when large it is comparatively pale, and the concentration of the peroxide in the vapour space will vary accordingly. Hence, the pressure of the oxygen should increase when a large proportion of the tube is occupied by the liquid. As this only holds good to a certain point (when the maximum on the curve is reached), it would appear probable that one of the above assumptions is incorrect. The equilibrium may be one between decomposition of certain molecules only present in the vapour, and recombination with formation of ordinary nitric acid proceeding in the liquid, or both liquid and vapour. Hence, when a large proportion of acid is present, the reversal becomes relatively greater than the decomposition; hence the diminution in the pressure of oxygen. The problem is also complicated by the fact that some of the peroxide will be present in the form of the simpler molecules of NO_2, and by the irregular exposure to light during day and night, which cannot be strictly compared to a constant temperature in dissociation.

Probably experiments in which known quantities of the peroxide were added to the acid before exposure would clear up some of the uncertainties, but it is not the intention of the authors to proceed further in this direction.

EXPERIMENTAL.

Preparation of the Acid.

Commercial pure acid (D 1·42) was freed from nitrogen peroxide by treatment with carbamide, chromic acid, or potassium permanganate, and was distilled in a vacuum in artificial light, or it was mixed with its own volume of concentrated sulphuric acid just before the distillation, when the anhydrous acid was desired. The three reagents named appear to be equally effective in purifying the acid, and no difference could be detected in the product.

The glass distilling flask, condenser, and receiver were fused together. The inlet to the flask, consisting of a thistle funnel with 1 mm. cross-bore tap in the stem, was fused through the top of the flask. The outlet from the receiver consisted of a long-drawn-out capillary, the tip of which was broken and re-sealed each time a fraction was removed. Although the flask contained scrap platinum, distillation usually proceeded without ebullition when the flask was immersed in warm water.

It was found impossible to remove nitrogen peroxide from nitric acid by fractionation; its removal must therefore be effected as above. Its presence is conveniently detected by diluting the sample to 10 per cent. and adding a few drops of potassium iodide or *m*-phenylenediamine, which should scarcely colour the sample. Exposure of concentrated colourless acid to diffused daylight or near a Nernst lamp for one hour induces a noticeable decomposition.

Examination of the Decomposition Products.

Berthelot measured the decomposition by opening the vessel over water, and determining the volume of oxygen. The present authors find that there is only one way in which this can be done without introducing large errors. If the tube is under diminished pressure and the water rushes up through the acid, causing admixture, rapid recombination of the products occurs, the extent depending on the time and shaking, but three-fourths of the whole will readily and quickly re-unite when a flask is used.

Long, narrow tubes were therefore employed; after exposure they were held vertically, tip upwards, completely immersed in a tank of water, under a large glass funnel leading into a graduated glass cylinder; if the tube is under pressure, when the tip is fractured the excess of gas is expelled and collected, and no water enters; if under less than one atmosphere pressure, the water merely forms a layer on the top of the heavier acid without appreciable admixture, and recombination, therefore, does not take place.

Another method employed with tubes under diminished pressure is to open them over boiled and cooled nitric acid of the same strength; here no recombination occurs, and correct results are obtained. The accuracy of the results was tested by connecting an exposed flask by pressure tubing to a column of mercury at barometric height, noticing the fall on breaking the tip, and then pumping out the gas with a Sprengel pump. Two determinations of the density of the gas thus obtained gave 15·7 and 16·1.

A number of analyses of the gases obtained were made after collecting them over water as above by treating them with alkaline pyrogallate. In the case of 70 per cent. acid, from 97 to 98 per cent. of oxygen was indicated, whilst 100 per cent. acid gave about 99 per cent. Apparently a little nitrogen is formed by some secondary change in the former case, although it is extremely difficult to free the acid from dissolved nitrogen, even after violent shaking with broken glass in a vacuum. The nitrogen peroxide was determined by pouring the nitric acid solution into a large volume of dilute permanganate; after remaining half-an-hour it was titrated, when it always corresponded with the oxygen collected.

Conditions Affecting the Decomposition.

For comparison a series of tubes 12 inches long, closed at one end, and about 10 c.c. capacity were drawn out at the other end, calibrated, and filled to varying extents with the sample. They were exhausted while remaining in ice and water, sealed, and exposed whilst lying side by side on a sloping board on an open roof facing south. When no further change had been observed during several days, the tubes were removed at mid-day on a bright day (that is, before recombination had occurred), and were at once examined. The results are incorporated in the curves in Fig. 1, which are not strictly accurate when a very small proportion of concentrated acid is present owing to appreciable dilution of the acid by the water formed. The true curves should, at the left hand side, be somewhat outside those plotted.

Recombination of the Products in the Dark.

A number of similar tubes were one-tenth filled with the sample of acid, evacuated, sealed, and exposed side by side as before. When no further change occurred, they were withdrawn and placed in the dark; one of them was at once examined, and the others in turn after various periods of seclusion. The rate and extent of recombination in the case of 70, 85, and 100 per cent. acid is shown in the curves in Figs. 2 and 3 (pp. 135, 136).

It was found that many hours' violent agitation by attachment to a shaking arrangement did not affect the rate of recombination.

Spontaneous Decomposition of the Anhydrous Acid.

Three tubes half filled with the acid were kept in the dark for seven days. One was examined and found colourless, and no oxygen was present. After four weeks the two remaining tubes were colourless; after twelve weeks they were light yellow. After eighteen weeks one was examined; it was under a pressure of 0·67 atmosphere of oxygen. The other was examined after thirty-six weeks, and was found to be under a pressure of 2·66 atmospheres of oxygen.

Two similar tubes were one-fourth filled with the same acid simultaneously with the above. One of them after eighteen weeks was under 0·28 atmosphere pressure; the other, after thirty-six weeks, was under 1·05 atmospheres.

It would appear not unlikely that concentrated solutions of the acid would show very slight decomposition if kept for some years in the dark; the curves for the recombination in Fig. 2 seem to indicate that it would never be quite complete with acids of 70 per cent. strength and upwards.

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XV.—*Nitrites of the Alkylammonium Series. Part II. Propylammonium Nitrite and Butylammonium Nitrite and their Decomposition by Heat.*

By Prafulla Chandra Rây and Jitendra Nath Rakshit.

Propylammonium Nitrite.

The propylammonium chloride required for the present purpose was obtained by the reduction of propionitrile by alcoholic sodium. The resulting product was freed from ammonium chloride by extraction with alcoholic ether. The platinichloride was analysed. (Found, Pt=37·22. Calc., Pt=37·14 per cent.)

The nitrite was prepared by the usual method of interaction between the chloride and silver nitrite, and evaporation of the solution in a vacuum over sulphuric acid. A pale yellowish-green, limpid liquid was obtained:

0·2501 gave 0·3117 CO_2 and 0·2115 H_2O. C=33·99; H=9·04.
0·0520 „ 6·5 c.c. N_2 (nitritic: moist) at 36° and 760 mm. N=13·12.

C_3H_9N,HNO_2 requires C=33·96; H=9·43; N(nitritic)=13·41 per cent.

Decomposition by Heat.—The substance decomposes very slowly, even at the ordinary temperature (32°), and minute bubbles are continuously given off in the vacuum of a Sprengel air-pump; a persistent click is thus hardly obtained. On raising the temperature, the rate of decomposition increases, and at 70° it is fairly regular and moderately rapid. The products of decomposition are mainly nitrogen, *iso*propyl alcohol, and water; small quantities of nitrosodipropylamine, and in some cases nitric oxide and free propylamine, were also detected. The oily drops which condensed in the upper cooler part of the tube responded to the Liebermann test. The liquid which passed over in the collecting tube was oxidised by chromic acid mixture and subjected to distillation. The presence of acetone in the distillate was proved by the iodoform test, and was evidently due to the *iso*propyl alcohol.

Linnemann (*Annalen*, 1872, **161**, 44), who also prepared propylammonium nitrite in solution, found that on distilling it, the resulting alcohol was not the normal one, but its isomeric modification. He also obtained a notable proportion of nitrosodipropylamine, the production of which he explained by the following equation:

$$2C_3H_7{\cdot}NH_3{\cdot}NO_2 = (C_3H_7)_2N{\cdot}NO + N_2 + 3H_2O.$$

It has been noticed that whenever nitric oxide is one of the gaseous products of decomposition, free amine is also simultaneously given off, and a residue of a nitrate is left behind, which is quite stable, even at 100°. Evidently the decomposition proceeds in three directions:

(1) $C_3H_7{\cdot}NH_3{\cdot}NO_2 = C_3H_7{\cdot}OH + N_2 + H_2O$.
(2) $2C_3H_7{\cdot}NH_3{\cdot}NO_2 = (C_3H_7)_2N{\cdot}NO + N_2 + 3H_2O$.
(3) $3C_3H_7{\cdot}NH_3{\cdot}NO_2 = C_3H_7{\cdot}NH_3{\cdot}NO_3 + 2NO + 2C_3H_7{\cdot}NH_2 + H_2O$.

Butylammonium Nitrite.

The method of preparation was exactly analogous to that of its lower homologues.* A syrupy, greenish-yellow liquid was obtained:

0·2690 gave 0·3970 CO_2 and 0·2430 H_2O. C = 40·21; H = 10·16.
0·3066 „ 33·0 c.c. N_2 (nitritic: moist) at 30° and 760 mm. N = 11·64.
$C_4H_{11}N,HNO_2$ requires C = 40·00; H = 10·00; N(nitritic) = 11·66 per cent.

Decomposition by Heat.—In the vacuum of the Sprengel air-pump the substance gives off minute bubbles at the ordinary temperature (32°), and the "click" is then stopped. On raising the temperature, the rate of decomposition increases, and at about 75° it becomes moderately regular. The whole of the nitrite was decomposed at this temperature. An oily liquid was seen to flow back in the cooler part of the tube, and it gave the Liebermann reaction. The gaseous product consisted of pure nitrogen, and the liquid which condensed in the collecting tube no doubt contained *iso*butyl alcohol, as found by Linnemann (*Annalen*, 1872, **162**, 5). It is worthy of note that the amine nitrites of the alkyl series give as the gaseous product of decomposition sometimes pure nitrogen and sometimes a mixture of nitrogen and nitric oxide; the presence of the latter gas is invariably associated with the liberation of free amine and the conversion of a corresponding portion of the amine nitrite into nitrate, as explained in the previous instance.

The determination of the degree of ionisation of methylammonium nitrite, based on the cryoscopic method, showed that it was of the same order as that of the alkaline nitrites (this vol., p. 1018).

The electrical conductivity of butylammonium nitrite has been measured by Mr. N. R. Dhar, B.Sc., of this laboratory, and the data obtained by him are given below:

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* An analysis of the butylammonium platinichloride gave Pt = 35·81; Calc. Pt = 35·15 per cent.

Dilution, v (in litres).	Molecular conductivity, μ_v.	Ionisation per cent. $\mu_v/\mu_\infty \times 100$.
16	3·33 K	67·9
32	3·37 K	68·8
128	3·68 K	75·0
256	4·0 K	81·0
512	4·2 K	85·7
1024	4·5 K	91·8
2048	4·9 K	100·0
4096	4·49 K	—

Here K is the cell constant; the value of K was determined from time to time in the course of the experiment, and was found practically constant.

The temperature during the observation was 31·7°; the maximum variation was only 0·1°. It is found, however, that at similar dilutions this nitrite is about 15 per cent. less ionised than barium nitrite, a typical member of the alkaline earth nitrites.

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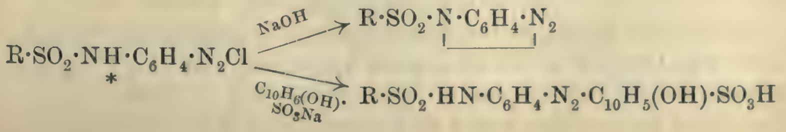
XVI.—*Amino-derivatives of Arylsulphonanilides and Arylsulphon-β-naphthalides.*

By Gilbert T. Morgan and Frances M. G. Micklethwait.

Earlier investigations have shown that the arylsulphonyl derivatives of *p*-phenylenediamine and its homologues when treated with nitrous acid yield para-diazoimides, which combine additively with phenols and the more reactive aromatic amines, forming azo-compounds (Trans., 1905, **87**, 1305; *J. Soc. Dyers*, 1909, **25**, 107). The experiments described in the present communication had for their object the preparation of amino-arylsulphonamides capable of yielding soluble azo-colouring matters with various naphthol- and naphthylamine-sulphonic acids.

When a para-diazoimide is employed for this purpose it is first converted into the corresponding diazonium salt, and this is added to the alkaline solution of a naphtholsulphonic acid. If, however, the velocity of coupling is relatively small, a considerable amount of the diazoimide is regenerated, and the yield of azo-dye is diminished to a corresponding extent:



$$\mathrm{R{\cdot}SO_2{\cdot}N\underset{*}{H}{\cdot}C_6H_4{\cdot}N_2Cl}\begin{cases}\xrightarrow{\mathrm{NaOH}} \mathrm{R{\cdot}SO_2{\cdot}\underbrace{N{\cdot}C_6H_4{\cdot}N_2}}\\ \xrightarrow[\mathrm{SO_3Na}]{\mathrm{C_{10}H_6(OH)\cdot}} \mathrm{R{\cdot}SO_2{\cdot}HN{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_5(OH){\cdot}SO_3H}\end{cases}$$

This difficulty may be overcome in several ways; one of these involves the replacement of the labile hydrogen atom (*) of the diazonium salt by an alkyl group, and another consists in employing meta-aminosulphonamides instead of the para-isomerides, because the diazonium salts of the former series do not yield diazoimides in neutral or alkaline solutions.

The arylsulphonyl derivatives of the *m*- and *p*-nitroanilines (compare D.R.-P. 157859) can be readily alkylated by heating alcoholic solutions of their alkali salts with alkyl iodides. The products yield on reduction the required *as*-arylsulphonylalkylphenylenediamines, the diazonium salts of which couple quantitatively with naphtholsulphonic acids.

In the naphthalene series the starting point was the well defined arylsulphonyl derivatives of β-naphthylamine, which have already been shown by the Aktiengesellschaft für Anilin-Fabrikation to furnish mononitro-derivatives with remarkable facility (D.R.-P. 164130). We now find that the sulphon-β-naphthalides give rise to dinitro-derivatives with equal readiness, so that these compounds afford a means of obtaining many intermediate products for the preparation of azo-dyes. Moreover, our experiments show that the sulphonic acids of β-naphthylamine can be utilised in a similar way. β-Naphthylamine-6-sulphonic acid, for example, furnishes a toluene-*p*-sulphonyl derivative which is readily nitrated, and the nitro-compound on reduction yields 2-*toluene*-p-*sulphonyl*-1:2-*naphthylenediamine*-6-*sulphonic acid*, which was isolated in the form of its sodium salt.

The alkylation of arylsulphonylnitro-β-naphthylamines is as readily effected as that of the arylsulphonanilides by heating their alkali salts with alkyl halides in alcoholic solution. The presence of a second nitro-group in the naphthalene nucleus, however, inhibits this reaction, so that the arylsulphonyldinitro-β-naphthylamines can be alkylated only through their silver salts, and even then the yield of alkyl derivative is comparatively small. The presence of a sulphonic group also inhibits methylation.

EXPERIMENTAL.

*Methylation of Toluene-*p*-sulphonylnitroanilines.*

Toluene-p-*sulphonylmethyl*-m-*nitroaniline*,

$$C_7H_7\cdot SO_2\cdot N(CH_3)\cdot C_6H_4\cdot NO_2.$$

—Twenty-two grams of toluene-*p*-sulphonyl-*m*-nitroaniline (Trans., 1906, **89**, 1292), 7 grams of sodium hydroxide, and 18—20 grams of methyl iodide were heated in 100 c.c. of alcohol for thirteen hours, the iodide being added slowly to prevent undue loss by evaporation.

After evaporating off the solvent, the residue was extracted with aqueous sodium hydroxide to remove any unaltered nitroanilide, and the insoluble product was crystallised from alcohol; it separated in pale brown prisms, melting at 114°:

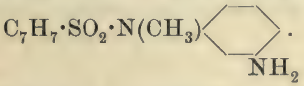
0·1448 gave 11·7 c.c. N_2 at 19° and 762 mm. N=9·33.
$C_{14}H_{14}O_4N_2S$ requires N=9·15 per cent.

Toluene-p-*sulphonylmethyl*-p-*nitroaniline* was prepared from toluene-*p*-sulphonyl-*p*-nitroaniline (Trans., 1906, **89**, 1303), using the same proportions of methyl iodide, sodium hydroxide, and alcohol as in the case of its isomeride—the preceding compound. The heating was, however, more prolonged, as the alkylation seemed to proceed more slowly. The product, which crystallised from alcohol in colourless prisms, melted at 182°:

0·2830 gave 23·0 c.c. N_2 at 21° and 760 mm. N=9·30.
$C_{14}H_{14}O_4N_2S$ requires N=9·15 per cent.

The as-*Toluene*-p-*sulphonylmethylphenylenediamines and their Azo-derivatives.*

as-*Toluene*-p-*sulphonylmethyl*-m-*phenylenediamine*,



$C_7H_7{\cdot}SO_2{\cdot}N(CH_3){\cdot}C_6H_4{\cdot}NH_2$.

Twelve grams of toluene-*p*-sulphonylmethyl-*m*-nitroaniline were reduced by boiling for two to three hours with 9 grams of iron filings, and 450 c.c. of water acidified with 6 c.c. of strong hydrochloric acid. After neutralising with sodium carbonate, the liquid was filtered off, and the iron oxide precipitate extracted with hot alcohol. On dilution with water this extract yielded the base in colourless crystals. Further purification was effected through the hydrochloride, which separated from acidified solutions in colourless crystals having a silvery lustre:

0·2004 gave 15·7 c.c. N_2 at 19° and 770 mm. N=9·13.
0·1826 „ 0·1331 $BaSO_4$. S=10·01.
$C_{14}H_{16}O_2N_2S,HCl$ requires N=8·98; S=10·27 per cent.

The base set free from this salt was crystallised from benzene and light petroleum, when it separated in yellow, prismatic needles, melting at 115—116°, and darkening on exposure to air.

When diazotised and coupled with alkaline β-naphthol the foregoing hydrochloride yielded an *azo-β-naphthol* derivative,

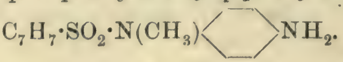
$$C_7H_7{\cdot}SO_2N(CH_3){\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH,$$

separating from benzene in clusters of orange-coloured, acicular crystals, melting at 185°:

0·1526 gave 13·7 c.c. N_2 at 23·5° and 767 mm. N = 10·18.

$C_{24}H_{21}O_3N_3S$ requires N = 9·74 per cent.

as-*Toluene*-p-*sulphonylmethyl*-p-*phenylenediamine*,



Twelve grams of toluene-*p*-sulphonylmethyl-*p*-nitroaniline were boiled for five hours with 400 c.c. of water, 10 c.c. of glacial acetic acid, and 20 grams of iron filings, the liquid being then neutralised with sodium carbonate, and filtered. Very little of the reduction product separated from the filtrate, the main portion being extracted from the iron oxide precipitate with hot alcohol. The base separated in large, colourless, ice-like crystals, and was further crystallised from benzene and light petroleum, when it was obtained in colourless, prismatic needles, melting at 142°:

0·2512 gave 22·5 c.c. N_2 at 20° and 762 mm. N = 10·28.
0·2483 „ 0·2172 $BaSO_4$. S = 12·00.

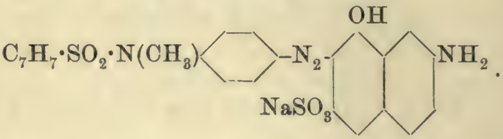
$C_{14}H_{16}O_2N_2S$ requires N = 10·14; S = 11·60 per cent.

The hydrochloride of this base, when diazotised and coupled with alkaline β-naphthol, gave an *azo-β-naphthol* derivative, which crystallised from benzene in red, prismatic needles, melting at 206°:

0·1344 gave 12·4 c.c. N_2 at 21° and 764 mm. N = 10·53.

$C_{24}H_{21}O_3N_3S$ requires N = 9·74 per cent.

Sodium Toluene-p-*sulphonylmethylamino*-p-*benzene-2-azo-7-amino-α-naphthol-3-sulphonate*,



as-Toluene-*p*-sulphonylmethyl-*p*-phenylenediamine (2·7 grams) was diazotised in 25 c.c. of 6 per cent. hydrochloric acid, and the solution added to 2·5 grams of 7-amino-α-naphthol-3-sulphonic acid (γ-acid) dissolved in aqueous sodium carbonate. After twelve hours the azo-compound was salted out, and recrystallised from water, when it separated in almost black, lustrous crystals:

0·1654 gave 15·2 c.c. N_2 at 22·5° and 767 mm. N = 10·46.
0·3366 „ 0·0406 Na_2SO_4. Na = 3·90.

$C_{24}H_{21}O_6N_4S_2Na$ requires N = 10·21; Na = 4·19 per cent.

This azo-dye gave brown shades of scarlet on wool or silk, and when diazotised yielded a crystalline, bronze-green diazo-compound, which coupled with β-naphthol-6-sulphonic acid to a bisazo-dye, furnishing reddish-brown shades on wool and silk. With α- and β-naphtholdisulphonic acids, chocolate-brown shades were produced, and 1:8-dihydroxynaphthalene-3:6-disulphonic acid gave very dark brown shades. These shades were not materially modified by subsequent chroming.

d-*Camphor-β-sulphonylmethyl*-p-*nitroaniline*,

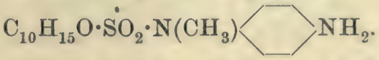
$C_{10}H_{15}O\cdot SO_2\cdot N(CH_3)\cdot C_6H_4\cdot NO_2$.

This compound, containing a hydroarylsulphonyl group, and the following base were prepared with the object of preparing optically active diazo-cyanides which might be useful in studying the stereoisomerism existing in this series of diazo-derivatives, but the only diazo-cyanide obtained was so unstable that this investigation was discontinued.

Twenty grams of *d*-camphor-β-sulphonyl-β-nitroaniline (Trans., 1905, **87**, 77) were methylated in 20 per cent. absolute alcoholic solution by boiling for ten hours with a moderate excess of methyl iodide and potassium hydroxide. After removing the solvent, the residue was extracted with aqueous sodium hydroxide, and the insoluble residue crystallised repeatedly from alcohol, when d-*camphor-β-sulphonylmethyl*-p-*nitroaniline* separated in long, colourless needles, melting at 177°:

0·1919 gave 12·8 c.c. N_2 at 19·5° and 765 mm. N = 7·73.
0·2484 „ 0·1655 $BaSO_4$. S = 9·14.
$C_{17}H_{22}O_5N_2S$ requires N = 7·66; S = 8·74 per cent.

d-*Camphor-β-sulphonylmethyl*-p-*phenylenediamine*,



The foregoing nitro-compound (6 grams) was reduced with 10 grams of iron filings, 240 c.c. of water, and 6 c.c. of glacial acetic acid. After boiling for thirty minutes the solution was neutralised, filtered hot, and the iron oxide precipitate extracted with warm alcohol. The basic product separated from both aqueous and alcoholic extracts, and was crystallised from benzene, when it was obtained in colourless, acicular prisms, melting at 109—111°:

0·2627 gave 18·4 c.c. N_2 at 17° and 775 mm. N = 8·33.
0·1635 „ 0·1159 $BaSO_4$. S = 9·73.
$C_{17}H_{24}O_3N_2S$ requires N = 8·33; S = 9·52 per cent.

The *azo-β-naphthol* derivative separated from alkaline solution as a bright scarlet precipitate, and when crystallised from hot alcohol melted at 170°.

d-Camphor-β-sulphonylmethylaminobenzene-*p*-diazonium chloride, sulphate, nitrate, and phosphate were very soluble in water; the perchlorate was precipitated from aqueous solution, but rapidly decomposed at the ordinary temperature. The diazo-cyanide separated as a yellow precipitate, which at the ordinary temperature changed rapidly into a red substance resembling shellac.

The Nitration of Toluene-p-*sulphonyl-β-naphthylamine.*

Toluene-*p*-sulphonyl-*β*-naphthylamine (m. p. 133°) was prepared by dissolving *β*-naphthylamine in warm dry pyridine, and adding rather more than the calculated amount of commercial toluene-*p*-sulphonyl chloride; the condensation was completed by gently boiling the mixture for an hour. This sulphon-*β*-naphthalide can also be obtained by heating together a mixture of equivalent proportions of *β*-naphthylamine, toluene-*p*-sulphonyl chloride, and fused sodium acetate, the mass being first moistened with toluene. Toluene-*p*-sulphonyl-1-nitro-*β*-naphthylamine (D.R.-P. 164130) was produced by adding 7 c.c. of nitric acid (D 1·42) to a suspension of 20 grams of toluene-*p*-sulphonyl-*β*-naphthylamine in 100 c.c. of glacial acetic acid, and shaking the mixture for about an hour. The yield was practically quantitative, and the product when recrystallised from alcohol separated in orange-yellow prisms, melting at 160—161°.

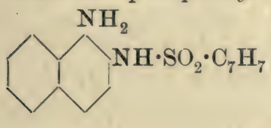
Toluene-p-*sulphonyl*-1 : 6-*dinitro-β-naphthylamine*,

$$C_7H_7 \cdot SO_2 \cdot NH \cdot C_{10}H_5(NO_2)_3,$$

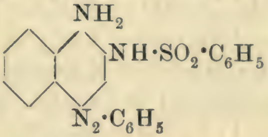
was produced with great facility, even under conditions in which the preceding compound might be expected. A quantitative yield was obtained by shaking together for two hours 20 grams of the sulphon-*β*-naphthalide, 100 c.c. of glacial acetic acid, and 14 c.c. of nitric acid (D 1·42). When crystallised from alcohol the dinitro-compound separated in colourless, felted needles, melting at 194°. This substance behaves as a strong acid; the alkali salts are soluble in water, and the ammonium salt crystallises in long, orange-red needles. The metallic salts are sparingly soluble in water; the copper compound is greenish-yellow, the nickel and cobalt derivatives are yellow, and the silver salt crystallises from dilute alcohol in transparent, amber-coloured prisms.

Toluene-*p*-sulphonyl-1 : 6-dinitro-*β*-naphthylamine was most readily hydrolysed by mixing with dilute sulphuric acid, and evaporating the mixture on the water-bath until the organic compound dissolved. Dilution with water then precipitated a yellow product, which separated from alcohol in golden-yellow crystals, melting at 241°. Although this substance apparently corresponded with 1 : 6-dinitro-*β*-naphthylamine (m. p. 242°), described by Gaess (*J. pr. Chem.*, 1891, [ii], **43**, 22), it contained less than the required amount of nitrogen. Prolonged evaporation on the water-bath with slightly diluted sulphuric acid transformed this product into a red compound, crystallising from glacial acetic acid in fern-like, red needles, also melting at 241°, and without depressing the melting point of the yellow substance. The red compound contains 17·84 per cent. of nitrogen, the theory for $C_{10}H_5(NO_2)_2{\cdot}NH_2$ being 18·02 per cent.; it is therefore a dinitro-β-naphthylamine, and as the isomeride melting at 239—242° is generally assumed to contain its nitro-groups in positions 1 and 6, we have accepted this view provisionally in the present communication, although the evidence stands in need of further confirmation (compare Gaess, *loc. cit.*; Graebe and Drew, *Ber.*, 1884, **17**, 1170; Loewe, *ibid.*, 1890, **23**, 2542).

2-*Toluene*-p-*sulphonyl*-1 : 2-*naphthylenediamine* (I):



(I.)



(II.)

Twenty grams of toluene-*p*-sulphonyl-1-nitro-β-naphthylamine suspended in 600 c.c. of water acidified with 20 c.c. of strong hydrochloric acid were reduced by boiling with 25 grams of iron filings for three hours. The precipitate was extracted successively with 200 c.c. of *N*-sodium hydroxide and hot water. The product was then precipitated from these extracts with dilute acetic acid, and crystallised from benzene, when it separated in snow-white, felted needles, melting at 187—189°. The base couples with diazonium salts, giving azo-derivatives, and is converted by nitrous acid into an ortho-diazoimide:

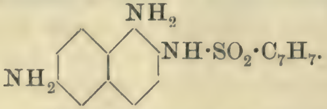
0·1676 gave 13·2 c.c. N_2 at 24° and 760 mm. N = 8·83.
0·2478 „ 0·1822 $BaSO_4$. S = 10·10.
$C_{17}H_{16}O_2N_2S$ requires N = 8·97; S = 10·25 per cent.

4-*Benzeneazo* - 2 - *benzenesulphonyl*-1 : 2-*naphthylenediamine* (II), prepared by coupling benzenediazonium chloride and 2-benzenesulphonyl-1 : 2-naphthylenediamine (Trans., 1910, **97**, 1714), crystallised from glacial acetic acid in orange-coloured, felted needles, and melted at 209—210°:

0·1206 gave 14·8 c.c. N_2 at 20° and 752 mm. N = 13·90.
$C_{22}H_{18}O_2N_4S$ requires N = 13·98 per cent.

This azo-compound, when treated with nitrous acid, was converted into a red diazoimide, which readily lost its benzenesulphonyl group on boiling with glacial acetic acid.

2-Toluene-p-*sulphonyl*-1 : 2 : 6-*triaminonaphthalene*,



Four grams of toluene-*p*-sulphonyl-1 : 6-dinitro-β-naphthylamine, dissolved in 200 c.c. of boiling alcohol and 30 c.c. of water, were reduced with 16 grams of zinc dust and 1·5 grams of ammonium chloride. The deep red coloration which developed at first disappeared, and the colourless solution was filtered rapidly into cold water. The precipitated triamine when crystallised from toluene separated in colourless, felted needles, melting at 190°:

0·1004 gave 11·4 c.c. N_2 at 23° and 756 mm. N=12·73.
0·1564 „ 0·1118 $BaSO_4$. S=9·79.
$C_{17}H_{17}O_2N_3S$ requires N=12·84; S=9·78 per cent.

The triamine was a somewhat oxidisable base, especially in the moist condition; it coupled with diazobenzenesulphonic acid, and gave rise to a yellow, sparingly soluble diazonium salt.

Methylation of Toluene-p-*sulphonyl*-β-*naphthylamine and its Nitro-derivatives.*

Toluene-p-*sulphonylmethyl*-β-*naphthylamine*,

$C_7H_7{\cdot}SO_2{\cdot}N(CH_3){\cdot}C_{10}H_7$,

was produced by boiling together in alcoholic solution for eight hours equivalent proportions of toluene-*p*-sulphonyl-β-naphthylamine, potassium hydroxide, and methyl iodide. The solution was concentrated to a small bulk and extracted with alkali hydroxide to remove unaltered toluene-*p*-sulphonyl-β-naphthylamine, and the insoluble residue crystallised from alcohol, when it separated in rosettes of colourless needles, melting at 77—78°:

0·3772 gave 0·2894 $BaSO_4$. S=10·53.
$C_{18}H_{17}O_2NS$ requires S=10·28 per cent.

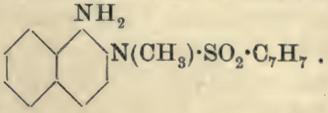
Toluene-p-*sulphonylmethyl*-1-*nitro*-β-*naphthylamine*,

$C_7H_7{\cdot}SO_2{\cdot}N(CH_3){\cdot}C_{10}H_6{\cdot}NO_2$.

—The preceding compound when warmed with two parts of nitric acid (D 1·4) in glacial acetic acid solution yielded principally a mononitro-derivative melting at 152—153°. The substitution of methyl for hydrogen in the toluenesulphonyl group greatly diminished the tendency to yield the dinitro-compound, although a small amount of the latter substance was produced.

The mononitro-compound was also prepared by methylating 18 grams of toluene-*p*-sulphonyl-1-nitro-β-naphthylamine (p. 148) with 3·4 grams of potassium hydroxide and 10 grams of methyl iodide in 80 c.c. of alcohol. After boiling for six to eight hours, the product had separated in colourless, glistening plates. Crystallisation from alcohol yielded the substance in colourless, flattened needles or prisms, melting at 152—153°. When exposed to light these crystals acquired superficially a distinctly green tint.

2-*Toluene*-p-*sulphonyl*-2-*methyl*-1 : 2-*naphthylenediamine*,



Twenty grams of the preceding compound suspended in 200 c.c. of alcohol and 20 c.c. of water were reduced by boiling for one to two hours with 27 grams of zinc dust and 4 grams of ammonium chloride. On dilution with water the cooled filtrate deposited the base, which when recrystallised from alcohol formed transparent prisms or needles, melting at 140—141°:

0·2418 gave 19·4 c.c. N_2 at 23° and 761 mm. N = 9·04.
0·2034 „ 0·1496 $BaSO_4$. S = 10·10.
$C_{18}H_{18}O_2N_2S$ requires N = 8·58; S = 9·81 per cent.

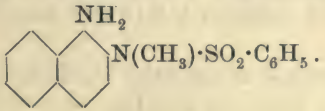
This diamine yielded a yellow diazonium salt, coupling readily with alkaline β-naphthol.

Benzenesulphonylmethyl-1-*nitro*-β-*naphthylamine*,

$$C_6H_5{\cdot}SO_2{\cdot}N(CH_3){\cdot}C_{10}H_6{\cdot}NH_2,$$

was prepared, like its toluene-*p*-sulphonyl homologue, by methylating benzenesulphonyl-1-nitro-β-naphthylamine (Trans., 1910, **97**, 1714) with a moderate excess of methyl iodide and potassium hydroxide in boiling alcoholic solution. It crystallised from alcohol in colourless needles, melting at 158—159°, and, like its homologue, it turned green on exposure to light.

2-*Benzenesulphonyl*-2-*methyl*-1 : 2-*naphthylenediamine*,



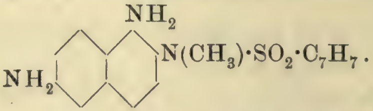
The preceding nitro-compound was reduced with zinc and ammonium chloride in the manner indicated for the preparation of 2-toluene-*p*-sulphonyl-2-methyl-1 : 2-naphthylenediamine. The diamine which was recrystallised from dilute alcohol separated in colourless plates or flattened needles, melting at 141—142°:

0·1304 gave 10·8 c.c. N_2 at 23° and 756 mm. N = 9·28.
0·2298 „ 0·1673 $BaSO_4$. S = 10·00.
$C_{17}H_{16}O_2N_2S$ requires N = 8·97; S = 10·25 per cent.

The base was readily soluble in dilute hydrochloric acid, and yielded a soluble yellow diazonium salt.

Toluene-p-*sulphonylmethyl*-1 : 6-*dinitro-β-naphthylamine*, $C_7H_7{\cdot}SO_2{\cdot}N(CH_3){\cdot}C_{10}H_5(NO_2)_2$. —Very little methylation took place when toluene-*p*-sulphonyl-1 : 6-dinitro-*β*-naphthylamine was heated in alcoholic solution with methyl iodide and potassium hydroxide. The silver salt of this dinitro-compound was therefore prepared from the ammonium salt and silver nitrate in aqueous solution. When suspended in alcohol and boiled with methyl iodide, the yellow silver salt slowly disappeared, and the alcoholic filtrate from silver iodide yielded on evaporation a mixture of unaltered silver salt and methyl derivative. The former substance was decomposed with hydrochloric acid, and removed in the form of the soluble ammonium and sodium salts; the latter when crystallised from alcohol separated in yellow, acicular prisms, melting at 180—181°. The yield of methyl derivative was about 50 per cent.

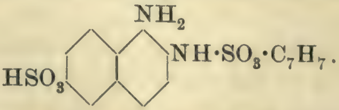
2-*Toluene*-p-*sulphonyl*-2-*methyl*-1 : 2 : 6-*triaminonaphthalene*,



The preceding compound was reduced in boiling 60 per cent. alcohol with excess of zinc dust and its own weight of ammonium chloride, and the solution of triamine filtered into iced water, when the product separated in granular form. The base when crystallised from a mixture of benzene and petroleum was obtained in lustrous, colourless, prismatic crystals, which blackened and decomposed at 185°:

0·1714 gave 19·0 c.c. N_2 at 22° and 747 mm. N = 12·33.
0·2310 „ 0·1635 $BaSO_4$. S = 9·72.
$C_{18}H_{19}O_2N_3S$ requires N = 12·31; S = 9·38 per cent.

2-*Toluene*-p-*sulphonyl*-1 : 2-*naphthylenediamine*-6-*sulphonic Acid*,



A slight excess of commercial toluene-*p*-sulphonyl chloride was slowly added to *β*-naphthylamine-6-sulphonic acid (Brönner acid) suspended in dry pyridine, and the mixture boiled until the amino-acid dissolved and no diazotisable substance remained. The solution was diluted with water, and the excess of pyridine boiled off. The solid residue, consisting of a pyridine salt of toluene-*p*-sulphonyl-β-naphthylamine-6-sulphonic acid, was nitrated by warming at 30° with 1½ parts of nitric acid (D 1·4) in seven parts of glacial acetic acid. The solution was diluted with water, and evaporated with sodium acetate until the nitro-derivative separated as a yellow, granular powder. Four grams of this product were reduced with 8 grams of iron filings, and 200 c.c. of water with 3 c.c. of concentrated hydrochloric acid. The solution rendered alkaline with sodium carbonate was filtered, acidified with acetic acid, and concentrated until the *sodium* salt of 2-toluene-*p*-sulphonyl-1 : 2-naphthylenediamine-6-sulphonic acid crystallised out. This product was again crystallised from water, and separated in grey, acicular prisms. A portion of these crystals, when decomposed with pure sulphuric acid, left on ignition a residue of sodium sulphate (½ mol.):

0·2718 gave 16·2 c.c. N_2 at 22° and 742 mm. N = 6·58.
0·2492 „ 0·2728 $BaSO_4$. S = 15·03.
$C_{17}H_{15}O_5N_2S_2Na$ requires N = 6·76; S = 15·45 per cent.

2-Toluene-*p*-sulphonyl-1 : 2-naphthylenediamine-6-sulphonic acid coupled with diazobenzenesulphonic acid and other diazonium salts. When treated with nitrous acid it yielded an ortho-diazoimide. This result demonstrates the constitution of the base, since it shows that the amino-group is in the ortho-position with respect to the toluene-*p*-sulphonamido-group.

An isomeric 2-toluene-*p*-sulphonyl-1 : 2-naphthylenediaminesulphonic acid was produced by adding 2-toluene-*p*-sulphonyl-1 : 2-naphthylenediamine hydrochloride dissolved in glacial acetic acid to cooled fuming sulphuric acid (25 per cent. SO_3). When the original red colour of the solution had disappeared, the liquid was poured on ice, the sulphuric acid precipitated with barium acetate, and the filtrate from barium sulphate concentrated to a small bulk. This sulphonic acid probably contains its sulphonic group in the para-position (4) with respect to the amino-group (1), since it does not couple with diazonium salts.

We desire to express our thanks to the Government Grant Committee of the Royal Society for a grant which has partly defrayed the expenses of this investigation.

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XVII.—*Electrolytic Reduction. Part V. Benzylidene Bases.*

By HERBERT DRAKE LAW.

PREVIOUS communications have been confined to the electrolytic reduction of aromatic compounds containing only one benzene nucleus. Well defined relations, varying regularly with a change of configuration, have been discovered, but in a somewhat limited field. It seemed desirable to extend this work to other compounds of the same type of formula as those previously investigated but capable of greater variation in constitution, and the benzylidene bases were selected for this purpose. These compounds are derived from the aromatic aldehydes, and have the same general formula, $R\cdot CH\colon X$. They differ chiefly in the fact that both the groups R and X may be modified in the benzylidene bases, but only the nucleus R in the aldehydes. It was anticipated that similar products of reduction would be obtained in the new field of research, which was amply confirmed by experiments. The work was greatly simplified by the fact that fewer reduced compounds were present in the reaction product. These were usually two in number, one being of a resinous nature and the other of the general formula $R\cdot CH_2\cdot XH$. A third substance was sometimes formed of the constitution $R\cdot CH(XH)\cdot CH(XH)\cdot R$, but no compounds involving the removal of the group X were ever present in weighable quantities. The substances formed corresponded with alcohols and hydrobenzoins of the previous investigations, but products similar in nature to the stilbenes were not isolated. The reactions taking place are summarised in the two following equations:

$$(1)\quad R\cdot CH\colon X + 2H = R\cdot CH_2\cdot XH.$$

$$(2)\quad 2RCH\colon X + 2H = R\cdot CH(XH)\cdot CH(XH)\cdot R.$$

EXPERIMENTAL.

The whole of the bases investigated were prepared in the same manner. A slight excess of amine was gradually added to the aldehyde, and the mixture gently warmed on the water-bath for thirty minutes. After cooling, the product was dissolved in ether and washed with small quantities of dilute acetic acid. The ethereal layer was then dried over anhydrous potassium carbonate, and the ether evaporated on the water-bath. The last trace of ether was removed under diminished pressure when necessary. The latter procedure was requisite only when the product could not be purified by fractional distillation, which was conducted whenever possible. The yield varied from 80 to 90 per cent. Five grams of the purified product were then dissolved in a mixture of 20 c.c. of ethyl acetate, 40 c.c. of alcohol, 20 c.c. of water, and 4 grams of potassium acetate, and reduced in the apparatus described previously (Trans., 1906, **89**, 1513). A current of 1 ampere was passed through the above mixture for two to three hours, and the temperature noted at the commencement and the finish of each experiment. The product was then diluted with two or three times its volume of water, and extracted with ether, the solvent removed on the water-bath, and the residue distilled in a current of steam for several hours. The distillate contained chiefly the secondary amine formed by reduction according to equation (1). There was also present a very small quantity of substance formed by the hydrolysis of the unreduced base. The quantity of this never exceeded 0·2 gram, and was worked up with the remainder of the distillate. The distillate was extracted with ether, the ether removed, and the residue converted into the hydrochloride by means of dilute hydrochloric acid. The residue in the distilling flask was then extracted with warm dilute hydrochloric acid to remove the last portions of the reduced base, when a green, resinous mass was left behind. This latter was collected, dried, and weighed. The two portions of the hydrochloride were mixed and evaporated to dryness on the water-bath, and also weighed. In this manner an almost complete separation of the two main products was effected. It was found to be impossible to shorten the process, although numerous modifications were tried. The hydrochloride was then purified by crystallisation from hot water containing a small quantity of hydrochloric acid. The pure free base was also obtained by the following method: a slight excess of sodium hydroxide was added, and the mixture gently warmed on the water-bath. This was next extracted with ether, the ether removed, and the residue finally distilled in a current of steam. The distillate was extracted with ether, and dried over anhydrous potassium carbonate. The ether was then removed on the water-bath, and the last trace absorbed in sulphuric acid under diminished pressure. The residue was finally distilled under atmospheric pressure to determine the boiling point. Some of the compounds obtained decomposed when distilled in an impure state, but not when treated as above. The process could be considerably shortened, however, in many cases.

The hydrochlorides of the above bases did not yield insoluble compounds with platinic or auric chlorides, and as a consequence the usual method of analysis could not be applied. Good analytical results were obtained by another quick and simple device, the essential features of which were as follows: 0·5 gram of the hydrochloride was mixed with 30 c.c. of water and 25 c.c. of *N*/10-sodium hydroxide. This was then warmed on the water-bath for ten minutes, cooled, and the free base extracted once with light petroleum. The petroleum extract was washed twice with water, and the washings added to the original aqueous mixture. The free alkali was then exactly neutralised with *N*/10-nitric acid, using methyl-orange as an indicator. The neutral solution was finally titrated with *N*/10-silver nitrate in the usual manner.

Benzylideneaniline.

Many preliminary experiments were conducted with benzylideneaniline to determine the best working conditions. It was soon found that the results were not influenced to any great extent by the degree of alkalinity of the solvent. The "nearly neutral medium" already described above (see also Trans., 1911, **99**, 1113) was finally adopted on account of its greater solvent power. A few experiments were also conducted with an electrolyte of sulphuric acid, but these were abandoned on account of the large amount of resin formation during reduction. The results of two experiments are given in the following table:

	Lead cathode.	Copper cathode.
Benzylaniline	4·2 grams	3·4 grams
Green resinous matter	0·05 gram	1·1 ,,
Temperature	15—25°	15—25°

The material of the cathode was the same as that described previously (*loc. cit.*). It will be seen from the above results that the total yield of product fell short of that required by theory. Larger scale experiments were conducted to determine the source of this discrepancy. The results then approximated more nearly to the theoretical value, but in addition to the above compounds small quantities of benzaldehyde and aniline were also isolated. These were present in almost equal quantities, accounting for nearly 4 per cent. of material. They were formed in all probability by the hydrolysis of the original benzylideneaniline. Dianilinodibenzyl was not found in the reduction product. Cathodes of lower supertension were also employed in the hope that the latter substance would be formed as in the analogous case of benzaldehyde (Trans., 1907, **91**, 754). Roughened platinum was first employed, but beyond reducing the velocity of the reduction, no marked change was noticed in products of the reaction. Finally, a platinised platinum electrode was employed, but in this case the supertension was too low to produce any reduction at all. It was concluded, therefore, that dianilinodibenzyl is not produced under the conditions of the above experiments.

Substituted Benzylideneanilines.

A few of the substituted benzylidene bases have been previously prepared, but not always accurately described. All of them possess one property in common. With bromine they yield a yellow additive product, insoluble in benzene and petroleum, but readily soluble in alcohol. These compounds could not be used for the purpose of identification, as no suitable solvent for crystallising them was discovered.

Methyl Derivatives of Benzylideneaniline.

Benzylidene-p-*toluidine*, $C_{14}H_{13}N$.—The boiling point of benzylidene-*p*-toluidine is given in the literature as 326°/723 mm. A large quantity of this substance was prepared, and purified by fractional distillation. When quite pure it boiled at 318°/775 mm. (Found, $C=86{\cdot}11$; $H=6{\cdot}65$. Calc., $C=86{\cdot}15$; $H=6{\cdot}66$ per cent.) The reduction of this substance on a lead cathode yielded products similar to those described for benzylideneaniline. A new product made its appearance when a copper cathode was utilised. The reaction mixture then contained an insoluble, crystalline substance, which was removed by filtration and treated separately. It was first dried and washed with successive small portions of hot alcohol, when a part of it dissolved. The residue was crystallised from amyl alcohol, and melted finally at 178—179°. The first alcoholic extracts deposited crystals on cooling, which on further treatment melted at 133°.

Compound melting at 133°:

0·1010 gave 0·3184 CO_2 and 0·0652 H_2O. $C=85{\cdot}97$; $H=7{\cdot}17$.

Compound melting at 178—179°:

0·1018 gave 0·3198 CO_2 and 0·0676 H_2O. $C=85{\cdot}67$; $H=7{\cdot}27$.

$C_{28}H_{28}N_2$ requires $C=85{\cdot}71$; $H=7{\cdot}14$ per cent.

0·5 Gram of each of these substances was treated on the water-bath for thirty minutes with 3 c.c. of concentrated nitric acid. A yellow, crystalline product (m. p. 91—93°) was obtained in each case, which was identified as benzil. The two original compounds, therefore, were isomeric di-*p*-toluidinodibenzyls, and had the constitution $C_6H_4Me{\cdot}NH{\cdot}CHPh{\cdot}CHPh{\cdot}NH{\cdot}C_6H_4Me$. The quantity of the above substances formed varied considerably with the temperature of the reduction, as the following table shows:

Mean temperature of reduction.........	16°	20°	24°	34°
Crystalline precipitate (in grams)......	0·2	0·5	0·7	1·3

The formation, therefore, is very similar to that in which hydrobenzoin is obtained from benzaldehyde (*loc. cit.*). Other compounds isolated were *benzyl*-p-*toluidine hydrochloride*, which crystallises in colourless needles melting at 181—182° (Found, HCl = 15·40. $C_{14}H_{15}N,HCl$ requires HCl = 15·63 per cent.), and *benzyl*-p-*toluidine*, an almost colourless oil, boiling at 319°/765 mm.:

0·1026 gave 0·3212 CO_2 and 0·0712 H_2O. C = 85·38; H = 7·71.
$C_{14}H_{15}N$ requires C = 85·28; H = 7·61 per cent.

The comparative results of reduction are given in the table on. p. 160.

Benzylidene-m-*toluidine*.—This was obtained as a pale yellow oil boiling at 315°/775 mm.:

0·1012 gave 0·3194 CO_2 and 0·0624 H_2O. C = 86·07; H = 6·86.
$C_{14}H_{13}N$ requires C = 86·15; H = 6·66 per cent.

The reduced product contained only resinous matter and *benzyl*-m-*toluidine*. The latter is a colourless oil boiling at 315—317°/760 mm.:

0·1024 gave 0·3200 CO_2 and 0·0682 H_2O. C = 85·22; H = 7·40.
$C_{14}H_{15}N$ requires C = 85·28; H = 7·61 per cent.

Benzyl-m-*toluidine hydrochloride* is a white, crystalline solid melting at 199—200°.

Found: HCl = 15·67. $C_{14}H_{15}N,HCl$ requires HCl = 15·63 per cent.

Benzylidene-o-toluidine.—This compound has been prepared previously by several investigators, but no agreement seems to have been arrived at with regard to its boiling point. It was obtained by the method already described, as an almost colourless oil boiling at 307—308°/775 mm. The reduction product contained chiefly benzyl-*o*-toluidine, melting at 62° (Rabant, *Bull. Soc. chim.*, 1891, [iii], **5**, 762, gives 56—57°). This latter substance yielded a hydrochloride melting at 165—166°. (Found, HCl = 15·67. Calc., HCl = 15·63 per cent.)

o-Tolylideneaniline.—This substance decomposed at its boiling point, especially when in an impure state. It was purified, therefore, by distillation in a current of steam, only the main portion of the distillate being retained. It was then an almost colourless oil:

0·1018 gave 0·3212 CO_2 and 0·0632 H_2O. C = 86·05; H = 6·88.
$C_{14}H_{13}N$ requires C = 86·15; H = 6·66 per cent.

The reduction product of the above substance contained chiefly *o-methylbenzylaniline*. The latter was crystallised from light petroleum, and obtained in colourless needles melting at 39°:

0·1151 gave 0·3604 CO_2 and 0·0781 H_2O. C=85·39; H=7·54.
$C_{14}H_{15}N$ requires C=85·28; H=7·61 per cent.

The *hydrochloride* melts at 176°.

Found: HCl=15·67. $C_{14}H_{15}N,HCl$ requires HCl=15·63 per cent.

m-*Tolylideneaniline.*—This compound decomposes at its boiling point, and was purified therefore like the previous substance. It was obtained as a pale brown oil:

0·1101 gave 0·3484 CO_2 and 0·0649 H_2O. C=86·03; H=6·55.
$C_{14}H_{13}N$ requires C=86·15; H=6·66 per cent.

m-*Methylbenzylaniline* was obtained by reduction, and when pure is a colourless oil boiling at 316—317°/770 mm.:

0·1045 gave 0·3264 CO_2 and 0·0712 H_2O. C=85·18; H=7·57.
$C_{14}H_{15}N$ requires C=85·28; H=7·61 per cent.

The *hydrochloride* melts at 179—180°.

Found: HCl=15·74. $C_{14}H_{15}N,HCl$ requires HCl=15·63 per cent.

p-*Tolylideneaniline.*—This is a pale yellow oil boiling at 318°/760 mm.:

0·1098 gave 0·3476 CO_2 and 0·0637 H_2O. C=86·34; H=6·47.
$C_{14}H_{13}N$ requires C=86·15; H=6·66 per cent.

The reduction product was composed largely of p-*methylbenzylaniline*, which crystallises from light petroleum in colourless needles melting at 47°:

0·1024 gave 0·3204 CO_2 and 0·0710 H_2O. C=85·22; H=7·68.
$C_{14}H_{15}N$ requires C=85·28; H=7·61 per cent.

The *hydrochloride* melts at 191°.

Found: HCl=15·67. $C_{14}H_{15}N,HCl$ requires HCl=15·63 per cent.

The following table shows the quantitative results of reduction of the six methylbenzylideneanilines already described. The conditions of the experiments were the same in each case as far as was possible with the simple apparatus at command. The temperature was difficult to regulate, and the attempt to keep it constant throughout an experiment was abandoned. In all the following cases the temperature was 15° at the commencement, and about 25° at the finish. It was assumed that the mean was 20° without further verification. The term "simple reduction product" refers to the formation of such substances as benzylaniline from benzylideneaniline, in which only single molecules of the reduced compound are involved. The heading "polymerised reduction products" is intended to recall the formation of dianilinodibenzyl and similar complexes. The two terms are fully explained by equations (1) and (2) respectively.

	Lead cathode.			Copper cathode.		
Substance reduced.	Simple reduction product, grams.	Polymerised reduction product.	Resin formation, gram.	Simple reduction product, grams.	Polymerised reduction product, gram.	Resin formation, grams.
Benzylideneaniline......	4·2	—	0·05	3·4	—	1·1
Benzylidene-*p*-toluidine	4·9	—	0·2	3·8	0 5	0·2
Benzylidene-*m*-toluidine	3·9	—	0·5	2·6	—	1·9
Benzylidene-*o*-toluidine	5·0	—	0·05	4·2	—	0·8
o-Tolylideneaniline ...	4·4	—	0·2	—	—	—
m-Tolylideneaniline ...	4·0	—	0·2	2·2	—	2·0
p-Tolylideneaniline ...	3·7	—	0·7	1·0	—	3·5

It is obvious from the above results that no high degree of accuracy has been attained. Most of the experiments were conducted on a much larger scale than that indicated in the table, and these confirmed the previous experience. The amount of resin formed represents the total matter insoluble in hydrochloric acid, and consequently is probably recorded with a fair degree of accuracy. It is noticeable that the largest amount of resin is formed in the case of *p*-tolylideneaniline, and diminishes rapidly as the methyl group moves in towards the centre of the molecule. The minimum is formed from benzylidene-*o*-toluidine, and then increases again as the methyl group leaves the centre of the molecule. The most interesting compound of all is benzylidene-*p*-toluidine. The resin formation in this latter case has diminished again, but a new type of compound has made its appearance, namely, *pp*-ditoluidinodibenzyl. It is probable that the formation of this compound offers a solution to the whole problem. It is noticeable also that the amount of resin formed increases as the potential of the reduction decreases, and is in agreement with previous results.

Chlorobenzylideneanilines.

p-*Chlorobenzylideneaniline.*—This substance has been described previously (Hantzsch and Schwab, *Ber.*, 1901, **34**, 832; v. Walther and Rätze, *J. pr. Chem.*, 1902, [ii], **65**, 263). The melting point is given as 66° and 62° respectively. When prepared by the method already described (*loc. cit.*), it crystallised readily from alcohol and melts at 65·5—66°. The reduction product contained chiefly p-*chlorobenzylaniline*, together with smaller quantities of a bright green, resinous substance. The reduced base is a pale yellow oil, which boils at 333—334°/765 mm., and remains liquid even on long keeping:

0·1140 gave 0·3002 CO_2 and 0·0544 H_2O. C=71·83; H=5·30.
$C_{13}H_{12}NCl$ requires C=71·72; H=5·52 per cent.

The *hydrochloride* melts at 211·5—212·5°.

Found: HCl=14·35. $C_{13}H_{12}NCl,HCl$ requires HCl=14·37 per cent.

m-*Chlorobenzylideneaniline*.—This is a colourless oil when freshly prepared, but on keeping it turns slightly yellow. It was purified by distillation in a current of steam:

0·1092 gave 0·2904 CO_2 and 0·0462 H_2O. C = 72·53; H = 4·70.

$C_{13}H_{10}NCl$ requires C = 72·39; H = 4·64 per cent.

The reduced product contained a green resin and m-*chlorobenzylaniline*. The latter is an almost colourless oil, boiling at 331—333°/765 mm.:

0·1070 gave 0·2808 CO_2 and 0·0540 H_2O. C = 71·57; H = 5·61.

$C_{13}H_{12}NCl$ requires C = 71·72; H = 5·52 per cent.

The *hydrochloride* is a white, crystalline substance melting at 190—191°.

Found: HCl = 14·42. $C_{13}H_{12}NCl,HCl$ requires HCl = 14·37 per cent.

o-*Chlorobenzylideneaniline*.—This has been prepared and the reduction products investigated by Bamberger and Müller (*Annalen*, 1900, **313**, 118). These authors obtained *o*-chlorobenzylaniline on reduction with sodium amalgam, and described the product as a pale olive-green oil decomposing on distillation. The electrolytic method of reduction yielded a similar green oil, which when treated by the method already described was separated into two constituents. One was a very pale green oil, and the other was an olive-green resin. The oil was distilled in a current of steam, and obtained quite colourless. It boiled at 325—327°/760 mm. without decomposition, but in other respects was identical with the *o*-chlorobenzylaniline prepared by the above investigators.

The following table summarises the results obtained with the chlorobenzylideneanilines:

	Lead cathode.		Copper cathode.	
Substance reduced.	Simple reduction product, grams.	Resin formation, gram.	Simple reduction product, grams.	Resin formation, grams.
p-Chlorobenzylideneaniline ...	3·2	0·8	2·9	2·2
m-Chlorobenzylideneaniline ...	3·9	0·6	2·0	2·5
o-Chlorobenzylideneaniline ...	4·4	0·17	4·2	0·7

These results agree substantially with those previously discussed. The amount of resinous matter formed diminishes as the substituted group is moved towards the centre of the molecule. The only result calling for attention is that of *m*-chlorobenzylideneaniline reduced on a copper cathode. The quantity of resin formed is slightly greater than that produced in the experiment immediately preceding. This may have been accidental. Unfortunately, the quantity of material at my disposal was too small to admit of these experiments being repeated.

Dimethylbenzylideneanilines.

p-*Tolylidene*-o-*toluidine*.—This substance was obtained in a pure state by distillation in a current of steam. It is a colourless oil boiling at 325—327°/765 mm., but readily decomposing if impure:

0·1050 gave 0·3320 CO_2 and 0·0684 H_2O. C = 86·28; H = 7·24.
$C_{15}H_{15}N$ requires C = 86·16; H = 7·18 per cent.

The reduced product contained p-*tolyl*-o-*toluidine* and a green resin. The former crystallises from light petroleum, and melts at 53°:

0·1054 gave 0·3298 CO_2 and 0·0766 H_2O. C = 85·33; H = 8·07.
$C_{15}H_{17}N$ requires C = 85·31; H = 8·06 per cent.

The *hydrochloride* is a colourless, crystalline substance, melting at 168·5°.

Found: HCl = 14·77. $C_{15}H_{17}N,HCl$ requires HCl = 14·74 per cent.

p-*Tolylidene*-m-*toluidine*.—This substance was obtained as a pale yellowish-brown oil:

0·1014 gave 0·3204 CO_2 and 0·0664 H_2O. C = 86·17; H = 7·27.
$C_{15}H_{15}N$ requires C = 86·16; H = 7·18 per cent.

The reduced product contained a green resin and p-*tolyl*-m-*toluidine*, which is a pale yellow oil boiling at 325—327°/760 mm.:

0·1028 gave 0·3214 CO_2 and 0·0752 H_2O. C = 85·26; H = 8·12.
$C_{15}H_{17}N$ requires C = 85·31; H = 8·08 per cent.

The *hydrochloride* melts at 181—182°.

Found: HCl = 14·77. $C_{15}H_{17}N,HCl$ requires HCl = 14·74 per cent.

p-*Tolylidene*-p-*toluidine*.—This substance crystallises from light petroleum in tufts of prisms melting at 92—93°:

0·1036 gave 0·3268 CO_2 and 0·0652 H_2O. C = 86·03; H = 7·10.
$C_{15}H_{15}N$ requires C = 86·16; H = 7·18 per cent.

The reduction product contained a green resin, p-*tolyl*-p-*toluidine*, and *di*-p-*toluidinodi*-p-*methyldibenzyl* in quantities varying very considerably with the conditions of the experiment. The latter substance separated from the reaction mixture on keeping, and was removed by filtration. The residual product was then worked up in the manner already described. The following table gives some of the results obtained:

	Lead cathode.		Copper cathode.	
Temperature of experiment:	15—20°	20—25°	15—20°	40—45°
Products of reduction:	Grams.	Grams.	Grams.	Grams.
1. Insoluble matter................	0·0	0·3	1·2	3·2
2. *p*-Tolyl-*p*-toluidine	4·6	4·4	2·9	0·8
3. Resin	0·2	0·5	0·5	1·0

p-*Tolyl*-p-*toluidine* is pale yellow, and melts at 60—61°:

0·1028 gave 0·3216 CO_2 and 0·758 H_2O. C=85·32; H=8·19.

$C_{15}H_{17}N$ requires C=85·31; H=8·06 per cent.

The *hydrochloride* melts at 165°.

Found: HCl=14·84. $C_{15}H_{17}N,HCl$ requires HCl=14·74 per cent.

The insoluble matter was purified by crystallisation from alcohol, and separated into two compounds, the less soluble melting at 175—177°, and the more soluble melting at 136—138°.

Substance melting at 175—177°:

0·1022 gave 0·3212 CO_2 and 0·0705 H_2O. C=85·71; H=7·76.

Substance melting at 136—138°:

0·1060 gave 0·3322 CO_2 and 0·0732 H_2O. C=85·47; H=7·69.

$C_{30}H_{32}N_2$ requires C=85·71; H=7·62 per cent.

Half a gram of each of the two above substances was heated on the water-bath with 3 c.c. of concentrated nitric acid for one and a-half hours. The product was diluted with water, and distilled in a current of steam. The yellow distillate was extracted with ether, and the extract washed with dilute sodium hydroxide solution. The ether was then removed, and the yellow, crystalline mass crystallised twice from light petroleum. The product melted at 100—102°, and was identical in all respects with *p*-tolyl. Another product formed in the above oxidation reaction was *p*-toluic acid. The two parent substances therefore probably had the constitution $C_6H_4Me{\cdot}NH{\cdot}CH(C_6H_4Me){\cdot}CH(C_6H_4Me){\cdot}NH{\cdot}C_6H_4Me$, and were stereoisomeric.

m-*Tolylidene*-m-*toluidine*.—This substance was obtained as a pale yellow oil decomposing at its boiling point:

0·1060 gave 0·3342 CO_2 and 0·0670 H_2O. C=85·99; H=7·09.

$C_{15}H_{15}N$ requires C=86·16; H=7·18 per cent.

The reduction product contained a green resin and m-*tolyl*-m-*toluidine*, which was a pale yellow oil boiling at 327—329°/760 mm.:

0·1094 gave 0·3424 CO_2 and 0·0802 H_2O. C=85·36; H=8·14.

$C_{15}H_{17}N$ requires C=85·31; H=8·06 per cent.

The *hydrochloride* melts at 196°.

Found: HCl=14·84. $C_{15}H_{17}N,HCl$ requires HCl=14·74 per cent.

m-*Tolylidene*-p-*toluidine*.—This is a pale yellow oil distilling slowly in a current of steam, but decomposing at its boiling point:

0·1026 gave 0·3246 CO_2 and 0·0652 H_2O. C=86·28; H=7·06.

$C_{15}H_{15}N$ requires C=86·16; H=7·18 per cent.

The reduction product obtained with lead cathodes was a mixture of a green resin and m-*tolyl*-p-*toluidine*. An insoluble, crystalline compound was also obtained when copper cathodes were employed.

m-*Tolyl*-p-*toluidine* is a colourless oil boiling at 324—326°/760 mm.:

0·1154 gave 0·3608 CO_2 and 0·0838 H_2O. C = 85·27; H = 8·08.
$C_{15}H_{17}N$ requires C = 85·31; H = 8·06 per cent.

The *hydrochloride* melts at 181—182°.

Found: HCl = 14·77. $C_{15}H_{17}N,HCl$ requires HCl = 14·74 per cent.

The insoluble compound was crystallised from alcohol, and finally melted at 177—179°:

0·1072 gave 0·3364 CO_2 and 0·0756 H_2O. C = 85·58; H = 7·83.
$C_{30}H_{32}N_2$ requires C = 85·71; H = 7·62 per cent.

A second substance was also present, but it could not be obtained in a pure state. The crude mixture and the pure compound were not converted into *m*-tolyl on oxidation with nitric acid, and in this respect resembled other similar meta-substituted compounds. It was most probably one of the isomerides of di-*m*-toluidinodi-*p*-methyldibenzyl. The quantity of material available was not sufficient for confirmatory experiments.

The following table shows the quantitative results obtained in the previous section. The headings of the columns have the same significance as before. The term "simple reduction product" refers to the compounds formed by the addition of two atoms of hydrogen at the double linking connecting the two benzene nuclei. The heading "polymerised" reduction product" indicates the products obtained by reduction, in which two of the original molecules become linked up at the nitrogen double linking.

	Lead cathode.			Copper cathode.		
Substance reduced.	Simple reduction product, grams.	Polymerised reduction product.	Resin, grams.	Simple reduction product, grams.	Polymerised reduction product, grams.	Resin, grams.
1. *p*-Tolylidene-*o*-toluidine	3·9	—	0·7	2·4	—	2·2
2. *p*-Tolylidene-*m*-toluidine	3·2	—	1·05	2·6	—	2·0
3. *m*-Tolylidene-*m*-toluidine	4·2	—	0·2	3·1	—	1·5
4. *p*-Tolylidene-*p*-toluidine	4·6	—	0·2	2·9	1·2	0·5
5. *m*-Tolylidene-*p*-toluidine	3·7	—	0·8	2·7	1·0	0·8

The results confirm those previously recorded. Least resin is formed when the substituted groups are distributed evenly in the two nuclei; thus the amount of resin formed in experiments 3 and 4 is considerably less than in the other cases. It is noteworthy that the resin formation is not the same for experiments 2 and 5, although the substituted groups occupy the *p*- and *m*-positions in each case. It is also noticeable that the amount of tarry matter formed in experiments 1 and 2, when lead cathodes were used, does not agree with that formed on copper cathodes. It is difficult to explain this discrepancy, but it may have been due to a slight alteration of the conditions of the experiments.

Chloromethylbenzylideneanilines.

p-*Chlorobenzylidene-o-toluidine.*—This substance has been prepared previously by v. Walther and Rätze (*loc. cit.*), who describe it as a crystalline substance melting at 35·5°. It was prepared in the manner already described, and crystallised from light petroleum. When quite pure it is a colourless solid, melting at 39°. It yielded p-*chlorobenzylaniline* and a green resin on reduction. The former is a pale yellow oil boiling at 335—337°/765 mm.:

0·1014 gave 0·2704 CO_2 and 0·0558 H_2O. C = 72·72; H = 6·11.
$C_{14}H_{14}NCl$ requires C = 72·58; H = 6·05 per cent.

The *hydrochloride* melts at 181—182°.

Found: HCl = 13·45. $C_{14}H_{14}NCl,HCl$ requires HCl = 13·62 per cent.

p-*Chlorobenzylidene*-m-*toluidine.*—This was obtained as a colourless solid, readily crystallising from light petroleum and melting at 28° (v. Walther and Rätze give 32°). The reduction product contained p-*chlorobenzyl*-m-*toluidine* and a green resin. The base crystallises readily from light petroleum, and melts at 38°:

0·1024 gave 0·2722 CO_2 and 0·0568 H_2O. C = 72·49; H = 6·16.
$C_{14}H_{14}NCl$ requires C = 72·58; H = 6·05 per cent.

The *hydrochloride* melts at 209—210°.

Found: HCl = 13·45. $C_{14}H_{14}NCl,HCl$ requires HCl = 13·62 per cent.

p-*Chlorobenzylidene*-p-*toluidine.*—By repeated crystallisation from alcohol this compound was obtained as an almost colourless solid melting at 128° (v. Walther and Rätze give 125°). It is sparingly soluble in cold alcohol, and could be reduced in quantities of 2·5 grams at a time only. The experiments were conducted at 35°. The product of reduction contained a green, resinous substance, p-*chlorobenzyl*-p-*toluidine*, and a complex, crystalline compound containing two joined molecules of the original compound. The free base melts at 47—48°.

0·1098 gave 0·2916 CO_2 and 0·0602 H_2O. C = 72·69; H = 6·09.
$C_{14}H_{14}NCl$ requires C = 72·58; H = 6·05 per cent.

The *hydrochloride* melts at 221—222°.

Found: HCl = 13·55. $C_{14}H_{14}NCl$ requires HCl = 13·62 per cent.

Two other products were present, but neither was obtained in a pure state. These melted respectively at 93—99° and 158—162°. They were probably the compound resulting from the union of two of the original molecules.

The following table summarises the results obtained with the chlorobenzylidenetoluidines:

	Lead cathode.			Copper cathode.		
Substance reduced.	Simple reduction product, grams.	Polymerised reduction product, gram.	Resin, grams.	Simple reduction product, grams.	Polymerised reduction product, gram.	Resin, grams.
1. *p.*-Chlorobenzylidene-*o*-toluidine	3·1	—	1·6	1·5	—	3·1
2. *p*-Chlorobenzylidene-*m*-toluidine	2·9	—	1·7	1·6	—	3·5
3. *p*-Chlorobenzylidene-*p*-toluidine	3·0	0·5	0·9	0·8	1·0	2·8

These results agree with those previously described. The weights given for experiment 3 are only a rough approximation, as it was found quite impossible to separate the products. This experiment was also conducted at 30—40°, and not under the same conditions as 1 and 2.

A very noticeable feature of the preceding work is the influence of the group substituted in the para-position on the products of reduction. All compounds containing the *p*-toluidine radicle readily polymerise on reduction, two molecules of the original compound being involved. The formation of these substances follows the same rules as those previously given (*loc. cit.*) for hydrobenzoins and others. The significance of this fact is difficult to interpret. It is also noticeable that the influence of substitution is different in the two nuclei involved.

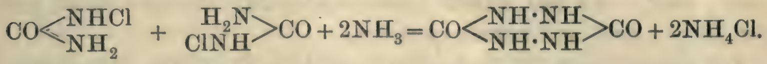
In conclusion, I wish to express my indebtedness to the Government Grant Committee for partly defraying the cost of the above work.

XVIII.—*The Formation of Dichlorocarbamide and its Behaviour Towards Amines.*

By Rasik Lal Datta.

The formation of *p*-urazine by the interaction of dichlorocarbamide and ammonia suggested an investigation as to the behaviour of the former with amines in general. This was further undertaken in order to test the truth of the assumption made by Chattaway (Trans., 1909, **95**, 235) that, previous to the formation of *p*-urazine, two molecules of monochlorocarbamide are first formed, which condense as below:

$$NHCl\cdot CO\cdot NHCl + NH_4\cdot OH = NH_2\cdot CO\cdot NHCl + NH_4\cdot OCl.$$



$$CO\Big<\begin{matrix}NHCl\\ NH_2\end{matrix} + \begin{matrix}H_2N\\ ClNH\end{matrix}\Big>CO + 2NH_3 = CO\Big<\begin{matrix}NH\cdot NH\\ NH\cdot NH\end{matrix}\Big>CO + 2NH_4Cl.$$

Dichlorocarbamide was prepared according to Chattaway's method (*Proc. Roy. Soc.*, 1908, *A*, **81**, 381). The poor yield obtained led to a search as to the conditions necessary to improve it, and although Chattaway later (Trans., 1909, **95**, 464) recommended the employment of zinc oxide as raising the yield to about 75 per cent., this, as will be shown later, appears erroneously to be ascribed to the arrest of hydrolysis due to hydrochloric acid.

Chattaway explains the formation of dichlorocarbamide as one of substitution of hydrogen for chlorine, giving rise to two molecules of hydrogen chloride, thus:

$$CO(NH_2)_2 + 2Cl_2 = CO(NHCl)_2 + 2HCl.$$

He further states that the filtrate from the dichlorocarbamide contains nothing but nitrogen chloride and ammonium chloride, the products of hydrolysis of dichlorocarbamide according to the equations:

$$CO(NHCl)_2 + H_2O = 2NH_2Cl + CO_2.$$
$$3NH_2Cl = 2NH_3 + NCl_3.$$

As is evident from the equations given above, much hydrogen chloride is formed, and it is claimed that this brings about the hydrolytic decomposition of dichlorocarbamide to such an extent that the yield amounts only to about 25 per cent. of the theoretical.

It has now been found that only a small part of the carbamide is available for chlorination, and there remains in the filtrate besides dichlorocarbamide and its hydrolytic products, much carbamide hydrochloride.

From the equation given above, it is evident that for each molecule of carbamide chlorinated there are formed two molecules of hydrogen chloride. This combines with carbamide to form the monohydrochloride, and although carbamide hydrochloride is readily dissociable in aqueous solution (Erdmann and Krutsch, *J. pr. Chem.*, 1842, **25**, 506), yet carbamide in this state cannot be converted into dichlorocarbamide. Furthermore, the dissociation of carbamide hydrochloride becomes negligibly small in the presence of a large excess of chlorine, so that the actual amount of carbamide that is available for chlorination is only one-third of that actually employed, as is evident from the equations:

$$CO(NH_2)_2 + 2Cl_2 = CO(NHCl)_2 + 2HCl.$$
$$2CO(NH_2)_2 + 2HCl = 2CO(NH_2)_2,HCl.$$

The yield theoretically possible is thus only 33·3 per cent. of the total carbamide, and the rest can be obtained as carbamide hydrochloride. The yield actually obtained by Chattaway was 25 per cent.; hence, the loss due to hydrolysis is only 7·6 per cent., and not 75 per cent. as Chattaway states.

The filtrate from the dichlorocarbamide is, in reality, almost pure carbamide hydrochloride, contaminated with only a small quantity of ammonium chloride due to the partial hydrolysis of dichlorocarbamide. Chattaway states that on evaporation of the filtrate, nitrogen chloride was given off and only ammonium chloride was left, but the residue which is left after moderate ignition is only cyanuric acid, mixed with ammonium chloride. It is important to note here that on ignition of carbamide hydrochloride, cyanuric acid is formed; since, however, cyanuric acid itself can be expelled by further ignition, the residue may have been, on this account, wrongly supposed by Chattaway to be pure ammonium chloride.

The mother liquor from the crystals of dichlorocarbamide was carefully evaporated on the water-bath, and it was observed that the residue never solidified completely. It was cautiously ignited over a flame, when it decomposed, with the evolution of white fumes of ammonium chloride. After carrying the ignition a little further and removing ammonium chloride by extraction with water, the residue was proved to contain cyanuric acid. (Found, N = 32·73. Calc., N = 32·56 per cent.)

As stated above, Chattaway in a later paper has shown that the yield can be improved to 75 per cent. by using zinc oxide, and he says that the neutralisation of the acid arrests the hydrolysis, but, as is evident, the increase in the yield is due to the liberation of carbamide from its hydrochloride, thus rendering it available for chlorination.

It has been shown by Wurtz (*Annalen*, 1847, **64**, 302) that when a dry current of chlorine is passed over molten carbamide, a vigorous reaction ensues, cyanuric acid, ammonium chloride, nitrogen and hydrogen chloride being obtained, and it was represented by him according to the following equation:

$$6CH_4ON_2 + 3Cl_2 = N_2 + 2HCl + 4NH_4Cl + 2C_3H_3O_3N_3,$$

in accordance with the combined results of heating carbamide hydrochloride and dichlorocarbamide.

In the course of my attempts to prepare dibromocarbamide, it was observed that a moderately concentrated solution of carbamide absorbs bromine on shaking, as appears from the discharge of the colour of the bromine, probably forming dibromocarbamide and carbamide hydrobromide in solution. The production of dibromocarbamide is rendered more probable by the fact that carbamide takes up only one-third of the weight of bromine that is actually required to brominate it completely. Hence, the other two-thirds of the carbamide may have been fixed as hydrobromide, confirming the theory put forward above.

Smolka (*Monatsh.*, 1887, **8**, 67) observed that when bromine is passed over heated carbamide, cyanuric acid, ammonium bromide, and nitrogen are formed, and expressed the reaction by the equation:

$$12CH_4ON_2 + 9Br_2 = 4C_3H_3O_3N_3 + 6NH_4Br + 12HBr + 3N_2;$$

but it is no doubt through the intermediate dibromocarbamide that the reaction takes place, and it is therefore really explained by the equation:

$$6CH_4ON_2 + 3Br_2 = N_2 + 2HBr + 4NH_4Br + 2C_3H_3O_3N_3.$$

Behaviour of Dichlorocarbamide with Amines.

The action of ammonia on dichlorocarbamide giving rise to the easy and interesting formation of *p*-urazine, a saturated solution of the former was allowed to react with amines in general. The result was unexpectedly interesting; instead of the precipitation of *p*-urazine, gases were evolved, and the solution acquired a distinct odour of chloroamines. This happened with the lower amines of the aliphatic series, but with benzylamine a white cloudiness, unaccompanied by the evolution of any gas, was the result, the opalescence soon resulting in a pale yellow liquid. If the amine is added to an excess of dichlorocarbamide, the liquid separated is found on analysis to be pure dichlorobenzylamine; but with a moderate quantity of dichlorocarbamide, monochloroamine is the product. Hence it is clear that the chlorine in dichlorocarbamide is very loosely combined, as was to be expected, for dichlorocarbamide is, in fact, a substituted nitrogen chloride.

The details of analysis and other decompositions of these chloroamines will form the subject of a separate communication.

I take this opportunity to express my best thanks to Professor P. C. Rây for his encouragement in carrying on the above investigation.

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XIX.—*The Transformation of Ammonium Cyanate into Carbamide.*

By Frederick Daniel Chattaway.

The course of the reaction which takes place when ammonium cyanate is transformed into carbamide has never been satisfactorily explained. Up to a few years ago it was universally regarded as a peculiar case of isomeric change, and no consideration was given to the process by which the conversion was effected.

Walker and Hambly (Trans., 1895, **67**, 746) then showed that the transformation was reversible, but that in aqueous solution it was accompanied by a subsidiary irreversible action, in which a portion of the cyanate was hydrolysed and converted into ammonium carbonate. From measurements of the velocity of transformation, they showed that the reaction was approximately bimolecular, and not unimolecular, as had up to that time been assumed, and concluded that the reacting atomic groups were the ammonium and cyanic ions produced by the electrolytic dissociation of the ammonium cyanate, and that the transformation should be formulated thus:

$$NH_4^{\cdot} + CNO' = CO(NH_2)_2.$$

It has been several times pointed out (compare Goldschmidt (*Zeitsch. Elektrochem.*, 1905, **11**, 5) that this conclusion is not justified, and that the results agree equally well with the assumption that it is the non-ionised portion of the ammonium cyanate which undergoes transformation. The view that the ions take no part in the reaction is strengthened by Walker and Kay's observation (Trans., 1897, **71**, 489) that ammonium cyanate, when dissolved in 90 per cent. ethyl alcohol, is converted into carbamide about thirty times as fast under similar conditions as when dissolved in pure water. As the alcohol diminishes the degree of dissociation of the cyanate, and should therefore diminish the rate of carbamide-formation if this is due to the ions, Walker and Kay are forced to assume that the alcohol increases the rate at which the ions interact to an extent much more than counterbalancing their diminished number, so that on the whole an accelerative effect is produced.

Further evidence that ammonium and cyanic ions are not necessarily involved in the transformation is found in the circumstance that pure dry solid ammonium cyanate passes over into carbamide when heated; for example, Walker and Kay (*loc. cit.*) found that it is almost wholly transformed into carbamide when heated at 61°

for five hours, a small quantity of ammonia and cyamelide being formed at the same time whilst between 76° and 89°, the exact temperature depending on the rapidity of heating and state of aggregation, it transforms so rapidly that fusion takes place, followed almost immediately by resolidification, the solid mass now only re-melting at 128°, three degrees below the melting point of carbamide. In this rapid transformation, ammonia is given off freely.

We may conclude therefore with reasonable certainty that formation of carbamide is due to non-ionised ammonium cyanate.

The transformation of ammonium cyanate into carbamide appears to be a simple process until the atomic rearrangement consequent upon it is considered. It is then seen that if it is to be regarded as intramolecular, it is altogether unusual and exceptional.

The transformation of ammonium cyanate cannot, however, be regarded alone, but must be explained in a manner that brings it into line with other reactions in which carbamides are produced, or in which cyanic acid and the *iso*cyanates take part. Any theory which attempts to explain the formation of carbamide from ammonium cyanate must, besides the facts established by Walker and his co-workers, take the following into account:

1. That ammonia is always present while conversion is taking place.
2. That the *iso*cyanic esters are converted into mono-substituted carbamides by interaction with ammonia, and into symmetrical di-substituted carbamides by interaction with primary or secondary amines.*
3. That alcohol can react with cyanic acid, cyanates, and *iso*cyanic esters to form urethanes or carbamic esters.
4. That carbamide, when heated, yields biuret and finally cyanuric acid.
5. That carbamide, when heated with any aromatic primary amine, yields first a monosubstituted and finally a disubstituted carbamide.
6. That carbamic esters are formed when carbamide is heated with alcohols.
7. That cyanic acid and its esters polymerise on keeping.

These instances will suffice as examples of the types of reactions which appear to be closely related and to admit of a similar explanation. All these reactions can be simply explained and brought into harmony by regarding them as instances of the well-known tendency of the carbonyl group to add on groups, such as

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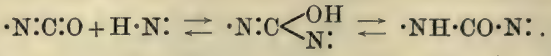
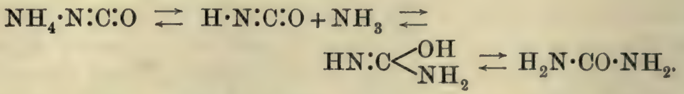
* The formation of *s*-disubstituted carbamides from the *iso*cyanic esters by the action of water is due to the hydrolysis of one portion of the ester and reaction of the remaining unchanged ester with the primary amine thus formed.

$\begin{smallmatrix}\mathrm{R}\\ \mathrm{R}\end{smallmatrix}{>}\mathrm{NH}$ or $\mathrm{R{\cdot}OH}$, followed by a subsequent atomic rearrangement involving only the transference of a hydrogen atom from an oxygen atom to a nitrogen atom connected with it through the doubly linked carbon atom, thus*:



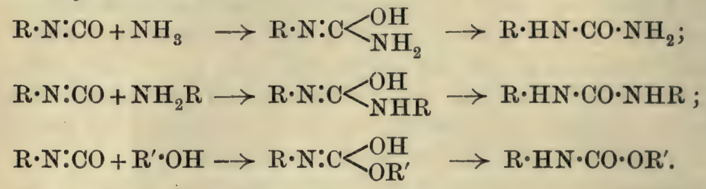
$$\mathrm{\cdot N{:}C{:}O + H{\cdot}N{:}} \rightleftarrows \mathrm{\cdot N{:}C}{<}\begin{smallmatrix}\mathrm{OH}\\ \mathrm{N{:}}\end{smallmatrix} \rightleftarrows \mathrm{\cdot NH{\cdot}CO{\cdot}N{:}}\,.$$

The conversion of ammonium cyanate into carbamide should therefore be formulated as follows:



$$\mathrm{NH_4{\cdot}N{:}C{:}O} \rightleftarrows \mathrm{H{\cdot}N{:}C{:}O + NH_3} \rightleftarrows \mathrm{HN{:}C}{<}\begin{smallmatrix}\mathrm{OH}\\ \mathrm{NH_2}\end{smallmatrix} \rightleftarrows \mathrm{H_2N{\cdot}CO{\cdot}NH_2}.$$

The *iso*cyanic esters are similarly converted into monoalkyl- and *s*-dialkyl-carbamides by ammonia and amines, and into carbamic esters by alcohols thus:



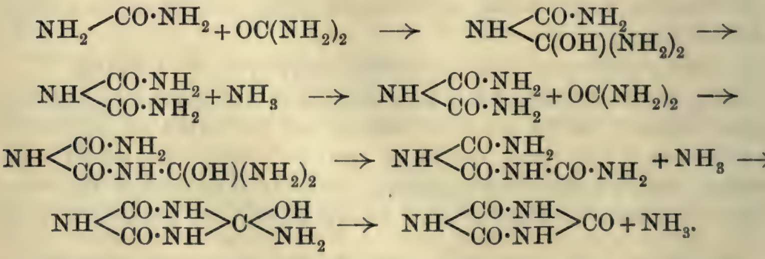
$$\mathrm{R{\cdot}N{:}CO + NH_3} \longrightarrow \mathrm{R{\cdot}N{:}C}{<}\begin{smallmatrix}\mathrm{OH}\\ \mathrm{NH_2}\end{smallmatrix} \longrightarrow \mathrm{R{\cdot}HN{\cdot}CO{\cdot}NH_2};$$

$$\mathrm{R{\cdot}N{:}CO + NH_2R} \longrightarrow \mathrm{R{\cdot}N{:}C}{<}\begin{smallmatrix}\mathrm{OH}\\ \mathrm{NHR}\end{smallmatrix} \longrightarrow \mathrm{R{\cdot}HN{\cdot}CO{\cdot}NHR};$$

$$\mathrm{R{\cdot}N{:}CO + R'{\cdot}OH} \longrightarrow \mathrm{R{\cdot}N{:}C}{<}\begin{smallmatrix}\mathrm{OH}\\ \mathrm{OR'}\end{smallmatrix} \longrightarrow \mathrm{R{\cdot}HN{\cdot}CO{\cdot}OR'}.$$

Tertiary amines not having a hydrogen atom attached to the nitrogen are not able to react in this manner. The action of alcohols on cyanic acid and the metallic cyanates to form urethanes and the action of water in hydrolysing cyanic acid and the cyanic esters are similar in type to the foregoing, as is also the behaviour of carbamide when heated alone or with alcohols or amines, and all can be similarly formulated.

When, for example, carbamide is heated alone, the amino-group of one molecule reacts with the carbonyl group of another; this is followed by the elimination of ammonia, biuret, and finally by a repetition of the process, cyanuric acid being produced, thus:



$$\mathrm{NH_2}{\diagup}\mathrm{CO{\cdot}NH_2 + OC(NH_2)_2} \longrightarrow \mathrm{NH}{<}\begin{smallmatrix}\mathrm{CO{\cdot}NH_2}\\ \mathrm{C(OH)(NH_2)_2}\end{smallmatrix} \longrightarrow$$

$$\mathrm{NH}{<}\begin{smallmatrix}\mathrm{CO{\cdot}NH_2}\\ \mathrm{CO{\cdot}NH_2}\end{smallmatrix} + \mathrm{NH_3} \longrightarrow \mathrm{NH}{<}\begin{smallmatrix}\mathrm{CO{\cdot}NH_2}\\ \mathrm{CO{\cdot}NH_2}\end{smallmatrix} + \mathrm{OC(NH_2)_2} \longrightarrow$$

$$\mathrm{NH}{<}\begin{smallmatrix}\mathrm{CO{\cdot}NH_2}\\ \mathrm{CO{\cdot}NH{\cdot}C(OH)(NH_2)_2}\end{smallmatrix} \longrightarrow \mathrm{NH}{<}\begin{smallmatrix}\mathrm{CO{\cdot}NH_2}\\ \mathrm{CO{\cdot}NH{\cdot}CO{\cdot}NH_2}\end{smallmatrix} + \mathrm{NH_3} \longrightarrow$$

$$\mathrm{NH}{<}\begin{smallmatrix}\mathrm{CO{\cdot}NH}\\ \mathrm{CO{\cdot}NH}\end{smallmatrix}{>}\mathrm{C}{<}\begin{smallmatrix}\mathrm{OH}\\ \mathrm{NH_2}\end{smallmatrix} \longrightarrow \mathrm{NH}{<}\begin{smallmatrix}\mathrm{CO{\cdot}NH}\\ \mathrm{CO{\cdot}NH}\end{smallmatrix}{>}\mathrm{CO + NH_3}.$$

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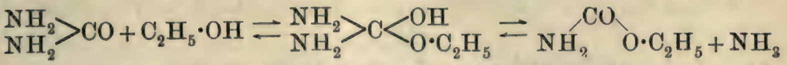
* Neglecting the precise mode by which this addition is effected, involving probably the residual affinity of both oxygen and nitrogen.

When carbamide is heated with alcohol, the action takes place thus:



$$\begin{matrix}NH_2\\NH_2\end{matrix}\!\!>CO + C_2H_5\cdot OH \rightleftharpoons \begin{matrix}NH_2\\NH_2\end{matrix}\!\!>C\!\!<\!\!\begin{matrix}OH\\O\cdot C_2H_5\end{matrix} \rightleftharpoons NH_2\diagup\!\overset{CO}{}\!\diagdown O\cdot C_2H_5 + NH_3$$

The production of substituted carbamides by heating carbamide itself with anilines, which, as the author has shown, is a general reaction for the preparation of monoaryl- and *s*-diaryl-carbamides, can be similarly formulated, thus:

$$R\cdot NH_2 + O{:}C(NH_2)_2 \rightleftharpoons RHN\cdot C(OH)(NH_2)_2 \rightleftharpoons RHN\cdot CO\cdot NH_2 + NH_3.$$

$$R\cdot NH_2 + O{:}C(NH_2)\cdot NHR \rightleftharpoons RHN\cdot C(OH)\cdot NH_2\cdot NHR \rightleftharpoons RHN\cdot CO\cdot NHR + NH_3.$$

The polymerisation of cyanic acid into cyanuric acid is the result of a similar action, cyamelide being formed by an analogous but more complicated process.

It therefore appears that what has hitherto been regarded as the oldest and best-known instance of isomeric change is not a case of isomeric change at all, but a reaction between cyanic acid and ammonia exactly analogous to the reactions between *iso*cyanic esters and ammonia or amines, whereby substituted carbamides are formed.

It is pointed out by Mr. D. L. Chapman in the appended note * that this view of the reaction is not inconsistent with the results obtained by Walker and his co-workers.

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* The view that carbamide is formed from ammonium cyanate by the interaction of the ammonia and the undissociated cyanic acid resulting from the non-electrolytic dissociation of the salt does not appear to be inconsistent with the fact experimentally established by Walker and his co-workers that the rate of formation of carbamide is proportional to the product of the concentration of the two ions provided that we may assume that the ions behave normally. For:

$$k_1[NH_3] = [NH_4^{\cdot}][OH']$$

and

$$k_2[HNCO] = [NCO'][H^{\cdot}]$$

whence

$$k_1k_2[NH_3][HNCO] = [NH_4][NCO'][OH'][H^{\cdot}]$$
$$= [NH_4][NCO']K_w \quad . \; . \; . \; . \; . \; . \; . \; . \quad (i)$$

From which it follows that the product of the concentrations of the ions is proportional to the product of the concentrations of the free ammonia and the undissociated cyanic acid in the solution. The fact that the addition of ammonia to a solution of ammonium cyanate does not appreciably affect the rate of conversion of the latter into carbamide does not invalidate the view of the change advocated by Chattaway, since, by increasing the concentration of the ammonia, the concentration of the undissociated cyanic acid is reduced. A deduction from the above argument ought to be noticed. From the relation

$$[NH_4][NCO'] = k[NH_4NCO]^n$$

(in which n is a constant greater than unity and k is also a constant) and the

XX.—*Copper Salts and their Behaviour with Alkalis.*

By SPENCER UMFREVILLE PICKERING, M.A., F.R.S.

IN searching for cupri-compounds suitable for the elucidation of those points which have been dealt with in previous communications (Trans., 1910, **97**, 1837; 1911, **99**, 169, 1347), the action of alkali on a number of copper salts was examined, and the results, which in many cases throw further light on the nature of these compounds, are embodied in the present communication. That those cupri-compounds wherein the copper is in the non-carboxylic portion of the molecule, contain it as CuOH displacing hydrogen in alcoholic hydroxyl, has already been established in such cases as have been examined, and that alcoholic groups are necessary for the formation of such compounds has now been proved, by finding that in the nineteen cases in which no such group is present, no cupri-salt is formed by the action of alkali, but a basic salt is precipitated instead; whereas in the thirteen other cases, where alcoholic hydroxyl groups are present, a cupri-salt is formed; sometimes accompanied with the formation of some basic salt also, in amounts depending on the proportion of water present.

The presence of alcoholic hydroxyl, however, should not necessarily be requisite for the formation of cupri-compounds with $:Cu^{IV}O$ in the carboxylic portion of the molecule, yet in no such case has a cupri-compound been obtained by the direct action of potassium hydroxide; and, apparently, the copper may take up this position owing to the presence of alcoholic hydroxyl, even when the latter remains unaffected (malate, citrate). Cupri-compounds have, however, been obtained by other means in the case of some acids containing no alcoholic hydroxyl (maleic, carbonic).

With a potassium cupri-salt of a monobasic acid, none of the copper can be in the carboxylic portion of the molecule, and such compounds are evidently less stable than those which contain some copper in the carboxylic position. This has already been noticed

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equation (i), it follows that the non-electrolytic dissociation of ammonium cyanate cannot be regulated by the law of mass. It must also be remembered that the opinion recently expressed by Walker in his Presidential Address to the Chemical section of the British Association, that in a strong electrolyte the ions behave normally and the undissociated portion of the salt abnormally, implies that the undissociated part exerts a pressure considerably greater than that calculated from its concentration, and that such an implication, if it can be justified, will obviously necessitate a drastic modification of the hitherto accepted concept of a molecule.

D. L. C.

in the case of the quinate, and other instances will be found in the case of the glycerate, lactate and salicylate. Potassium cupriglycollate, already described (*loc. cit.*), is, however, comparatively stable.

Preparation of the Normal Copper Salts.

The normal cupric salts, in cases where they were sparingly soluble, were prepared by adding an equivalent of the potassium or sodium salt to copper sulphate; in other cases, by dissolving copper carbonate in the acid, and precipitating by alcohol.

With the former method a sulphate compound is liable to be formed if the mixed liquids are evaporated (for example, saccharate and malate); in the latter, the precipitate often consists of an imperfect emulsion, which on exposure to air partly liquefies; this may be avoided by placing it promptly in small quantities in a vacuum.

A few hitherto unrecorded data respecting some of these salts may be mentioned.

Propionate.—A solution of copper carbonate in slight excess of propionic acid yields dark bluish-green crystals of the normal salt, similar to the product obtained by Strecker (*Annalen*, 1854, **92**, 89), but if the solution is neutral, tough, rounded masses of light blue, acicular crystals are obtained, consisting of

$$(C_3H_5O_2)_2Cu,CuO,$$

anhydrous at 100°, but retaining $1H_2O$ over sulphuric acid. The normal salt is too soluble to be prepared by double decomposition, as it cannot be washed free from sulphate without being almost entirely dissolved.

Methylsuccinate (*Pyrotartrate*).—A dark greenish-blue, minutely crystalline, and nearly insoluble salt, which loses all its water at 100°, instead of retaining it, as generally stated. A double salt, $(C_5H_6O_4)_3Cu_2K_2$ (anhydrous), has previously been mentioned (Trans., 1911, **99**, 810 *) as a product of the action of potassium methylsuccinate on copper acetate, and another, $(C_5H_6O_4)_2CuK_2$, with $3H_2O$, which it parts with at 100°, has recently been obtained. The main product of the reaction, however, is either normal copper methylsuccinate, or this salt mixed with a certain amount of basic salt. Enough copper passes into solution to form a deep blue liquid, from which one or other of the double salts separates, the former in greenish-blue, and the latter in violet-blue, crystals. These are decomposed by water, giving normal copper methylsuccinate. No double salt is formed by digestion of copper methylsuccinate with potassium methylsuccinate.

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* The words "pyrotartrate" and "protocatechuate" were accidentally transposed in the passage referred to.

On diluting and heating the liquid containing the double salts, a light blue basic salt containing nearly 2CuO is thrown down.

Fumarate.—A light blue solid retaining $2H_2O$ at 100°, which it parts with slowly at 150°.

Maleate.—This may be obtained either by double decomposition or by digestion of an equivalent of copper carbonate with maleic acid. In either case it forms small, hard, hexagonal plates of a very strong, rather dark blue colour, and agrees with the formula $C_4H_2O_4Cu,H_2O$. Büchner (*Annalen*, 1844, **49**, 60) obtained this salt by the action of maleic acid on copper acetate. It retains the water in a vacuum and at 100°, but loses nearly all ($0·8H_2O$) at 165—170°, and becomes of a fine, deep purple-blue colour, suggestive of its being, not an ordinary cupric salt, but a copper cuprimaleate (see Trans., 1911, **99**, 811).

When copper carbonate was treated in the cold with excess of maleic acid a crop of small, light blue, tetrahedral crystals was obtained, agreeing fairly well with the formula for an acid salt,

$$(C_4H_2O_4)_2CuH_2,8H_2O.$$

They lost $4H_2O$ at 100°, and the remainder of their water at 170°, becoming dark blue, but not purple like the normal salt. This is probably identical with the salt stated to be obtained by dissolving copper acetate in maleic acid.

A well crystallised double salt, $(C_4H_2O_4)_3Cu_2K_2$, with H_2O retained at 100°, has been mentioned (Trans., *loc. cit.*, p. 810).* It was obtained by dissolving copper acetate in a concentrated solution of potassium maleate, and evaporating the deep blue liquid formed.

Found: Cu = 22·48; K = 13·95. Ratio = 1 : 1·01.

$(C_4H_2O_4)_3Cu_2K_2$ requires Cu = 22·49; K = 13·83 per cent.

On other occasions the evaporation of the liquid yielded an uncrystallisable syrup, from which alcohol precipitated a very fine emulsion, which on drying gave values corresponding with $(C_4H_2O_4)_2CuK_2,CuO$: this, from its great solubility, cannot be a basic salt, but is, no doubt, a cupri-compound, with a constitution similar to that of the cuprimalate (p. 186). It is decomposed by water, some of the copper going into solution, and the rest being thrown down as a light blue basic salt.

Glycerate.—Copper glycerate presents features of great interest. When a solution of the carbonate in glyceric acid is precipitated by alcohol, only a portion of the copper is thrown down; but the precipitation may be completed by the addition of ether. The precipitate is generally in the form of a viscid mass, but under certain conditions it may be obtained as an emulsion. After washing with alcohol and drying rapidly in a vacuum, it may be heated at 100°.

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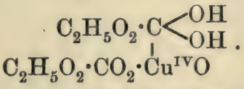
* Where there is a misprint of "malate" for "maleate," and of "$(C_3H_2O_4)$" for "$(C_4H_2O_4)$."

There is a very small further loss of water at 125°, above which temperature decomposition begins, and becomes considerable at 160°. On exposure to air the dried salt remains quite constant in weight. Five different preparations dried at 125° gave, respectively, Cu = 21·41, 21·02, 21·43, 20·90, 21·18: mean, 21·19, which agree fairly well with the monohydrate, $(C_3H_5O_4)_2Cu,H_2O$. (Calc., Cu = 21·72 per cent.).*

The solubility of this salt is practically infinite; but when a solution of it is kept for a day or more, a mass of small, light blue crystals separates, and continues to do so even after some weeks. These on drying lose only a trace of water, and suffer no decomposition at 160°. On exposure to air, no alteration in weight occurs. Analyses of four preparations gave Cu = 22·54, 22·66, 22·79, 22·84: mean, 22·71, showing it to be anhydrous copper glycerate (Cu = 23·23 per cent.), the values, as in the previous case, being about 0·5 per cent. below the calculated. It is soluble to the extent of 1·23 grams (= 0·28 gram Cu) in 100 c.c.†

It seems clear that the relationship of the two compounds cannot be that of an anhydrous salt to its monohydrate; a highly soluble hydrated salt could never be dehydrated by dissolving it in water; added to which, the supposed monohydrate cannot be deprived of its water without complete decomposition. A difference in constitution can be assigned, however, by representing the anhydrous compound as normal copper glycerate, and the other as a cupriglycerate, analogous to the cupritartrates, etc., previously described; thus:



$$\begin{array}{l} \mathrm{C_2H_5O_2{\cdot}C{<}^{OH}_{OH}} \\ \qquad\quad | \\ \mathrm{C_2H_5O_2{\cdot}CO_2{\cdot}Cu^{IV}O} \end{array}.$$

This view is further supported by the fact that the molecular colour-intensity of the cupriglycerate in solution (the precipitate obtained by alcohol) is three times greater than that of the normal copper glycerate, an increased depth of colour being one of the characteristics of cupri-compounds. These two substances are capable of existing independently as such in the dissolved condition; and, moreover, the cupriglycerate when in solution may be converted by heat into the normal copper glycerate, a solution of it when boiled having three times less colour-intensity than it had before, and remaining permanently lighter. The details of these observations are reserved for a further communication dealing with the colour of copper compounds generally.

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* One sample, which separated very slowly from the alcoholic liquid, contained an additional $6H_2O$ at 100°, losing it at 125°.

† The normal salt was prepared by Huppert (*Chem. Centr.*, 1863, 835) and by Garzarolli (*Annalen*, 1876, **182**, 190) by the interaction of lead glycerate and copper sulphate.

A concentrated solution of cupriglycerate when heated for some time over a water-bath yields a light blue precipitate containing Cu = 27·91 after drying at 100°, probably consisting of

$$[(C_3H_5O_4)_2Cu]_3,CuO,$$

which requires Cu = 28·24 per cent. It dissolves to a certain extent in water, begins to decompose at 125°, and on exposure to air gains weight, and becomes darker. It was not further investigated.

Malate.—With a suitable strength of solution, this, made from the carbonate and acid, may be precipitated by alcohol and dried in the manner mentioned above, without melting; but if the solution is too strong it is precipitated as a viscid mass. After being dried at 100° the salt agrees with the formula

$$(C_4H_4O_5Cu)_2,H_2O,$$

the water not being entirely eliminated below 150°, above which temperature decomposition begins.

It dissolves easily and quickly in water, but the solution, whether concentrated or dilute, deposits after a time a crystalline basic salt. On heating, also, this same basic salt gradually separates in comparatively large, bluish-green plates. After drying at 100°, three preparations of this salt gave the following numbers on analysis, the water being eliminated at 140°, beyond which temperature decomposition began:

	Percentage.		Ratio.
	Cu.	H_2O.	Cu : H_2O.
I.	33·73	11·56	1 : 1·21
II.	33·63	11·50	1 : 1·21
III.	33·64	—	— —
Calculated	32·77	11·14	1 : 1·2

The values calculated are for $(C_4H_4O_5Cu)_4,CuO,6H_2O$, but do not agree very well, except as regards the ratio, with those found.*

Aconitate.—By double decomposition a greenish-blue precipitate of $(C_6H_3O_6)_2Cu_3,2H_2O$ is obtained, after which dark green, hexagonal plates of $(C_6H_3O_6)_2Cu_3,3H_2O$ separate. This trihydrate is converted into the dihydrate at 165°.

A double salt, $C_6H_3O_6CuK$ (inadvertently described, *loc. cit.*, as an acid salt), was obtained by dissolving copper acetate in potassium aconitate solution, and evaporating. It formed large, blue, rhombic plates, becoming light blue at 100°, at which temperature it retained about $\frac{1}{2}H_2O$, which was liberated at 150°. Probably the salt is slightly decomposed by the water present during its preparation, for two different samples of it indicated a deficiency of potassium.

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* Acid and basic malates have been described (Hagen, *Annalen*, 1841, **38**, 257; Braconnot, *Ann. Chim.*, 1817, [ii], **6**, 239; Liebig, *Annalen*, 1838, **26**, 137; and Traube, *Zeitsch. Kryst. Min.*, 1899, **31**, 160), but it is doubtful whether the normal salt has been obtained hitherto. That obtained by Braconnot, which is described as such, was a green, amorphous salt, of which no analysis was made.

	Per cent.	Per cent.	Ratio.
Copper	22·50	12·49	1·00
Potassium...............	12·63	12·89	0·92
Water	3·86	—	0·61

No combination occurs when copper aconitate is digested with a solution of potassium aconitate.

Citrate.—When copper carbonate is dissolved in citric acid, the solution deposits after a time, or immediately on heating, a somewhat dark green, crystalline deposit, which, when dried in the air, consists of $(C_6H_5O_7)_2Cu_3,CuO,5H_2O$. At 100° it loses $3H_2O$, and turns to a light lavender-blue; this is the citrate of commerce. If, however, the freshly prepared solution is precipitated by alcohol, the normal salt is obtained; and this, after being dried rapidly in a vacuum, may subsequently be heated at 100° without decomposition. It retains $2H_2O$ at that temperature, and becomes anhydrous at 150°, decomposing at a slightly higher temperature. It dissolves easily and entirely in water, but the solution after a few minutes deposits a copious precipitate of light, greenish-blue needles, consisting of the basic salt in a nearly anhydrous condition (Found, Cu = 45·80. Calc., Cu = 46·38 per cent.), instead of the green hydrate previously described. If the emulsion of the normal salt, obtained on precipitation by alcohol, is left exposed to air, it liquefies, and then dries to a blue glass, which on heating, or on being kept for some time, decomposes into the basic salt. The emulsion, also, when left in the liquid from which it has been precipitated, begins to change into the basic salt after a few days.

The colour changes of the basic salt are remarkable, and are somewhat more complex than above stated. The green pentahydrate is converted in a vacuum into a light blue dihydrate, which on heating at 100° undergoes a well marked change to lavender-blue, without any further loss in weight. The peculiar colour of this compound suggested that it was really a copper cupricitrate, forming the final member of a series of which most of the other members had been isolated (Trans., 1910, **97**, 1847). To ascertain whether there was any difference in its heat of formation from that of the blue dihydrate, 4 grams of each were dissolved in 600 c.c. of a 10 per cent. solution of hydrochloric acid, when the molecular heats of dissolution were found to be, as a result of duplicate determination:

Blue salt..................	19,726 cal.
Lavender salt............	19,553 ,,

the difference is practically nil, as it represents errors of only 0·0017°.

The $2H_2O$ retained by this salt is probably constitutional water, as it is not eliminated below the decomposition temperature, 170°. The difference between the two forms may be of a similar nature to that between the two glycerates previously described.

The fact that the somewhat dark green pentahydrate becomes light blue on partial dehydration is remarkable, the general rule, so far as we are aware, being that when any such change occurs it is in the reverse direction, the copper salts being blue when hydrated, and turning green on dehydration.

Saccharate and *Mucate* (see Trans., 1911, **99**, 176).

Glycollate (see Trans., 1911, **99**, 1348).

Toluate.—The normal salt is a fairly light blue precipitate, obtained by double decomposition. Anhydrous at 100°.

Cinnamate.—A light blue precipitate obtained by double decomposition. It apparently contains some basic salt, as its copper content was 19·19, instead of 17·77 per cent.

Salicylate.—Piria (*Ann. Chim. Phys.*, 1855, [iii], **44**, 52) obtained the tetrahydrated normal salt by decomposing barium salicylate with copper sulphate.

When 10—15 grams of potassium salicylate are mixed with an equivalent of copper sulphate, the volume of the liquid being about 200 c.c., in a few minutes light, rather dirty blue, acicular crystals of the tetrahydrate begin to form.

Air-dried.—Found: Cu = 15·76. $(C_7H_5O_3)_2Cu,4H_2O$ requires Cu = 15·52 per cent.

Dried at 100°.—Found: Cu = 19·00. $(C_7H_5O_3)_2Cu$ requires Cu = 18·83 per cent.

If, in preparing it, the solutions were more concentrated, or were hot, a small quantity of a greenish-yellow, and almost insoluble, basic salt was first formed, after which the normal salt separated, either as the blue tetrahydrate or as a green (approximately) anhydrous salt (Found, Cu = 17·93. Calc., Cu = 18·83 per cent.), which latter on washing or exposure to moist air became changed into the blue tetrahydrate. The anhydrous salt sometimes changes spontaneously and suddenly in the liquid to the blue hydrated salt. Both forms of the normal salt dissolve to the extent of 0·17 gram (= 0·03 gram Cu) in 100 c.c., the solution being green, and its colour-intensity approximately seventeen times that of copper sulphate. On prolonged heating at 100° the salt loses some of its acid, and becomes brownish-yellow. A solution of it suffers no decomposition on boiling, but prolonged heating in an open dish leads to the loss of acid and the formation of a little basic salt, which, according to Piria, is $(C_7H_5O_3)_2Cu,CuO$.

In alcohol it dissolves to the extent of 4·7 grams of copper in 100 c.c., giving a very deep green solution, and from this on keeping there separates a crop of dark green crystals, consisting of an acid salt, $(C_7H_5O_3)_2Cu,C_7H_5O_3H$, which may be dried at 100° without sensible decomposition, provided the heating is not too prolonged. (Found, Cu = 13·43. Calc., Cu = 13·36 per cent.)

If some water is added to the alcoholic solution, the tetrahydrated normal salt gradually crystallises (Found, Cu = 15·70 on air-dried sample, 18·70 on that dried at 100°. Calc., Cu = 15·76 and 18·83 per cent.), but in green, rectangular plates, which rapidly become opaque, and are converted into a mass of the blue, acicular crystals constituting the ordinary form of the tetrahydrate.

When a large bulk of water is added to a strong alcoholic solution of the salicylate, a green, viscid mass is obtained, which soon solidifies. After washing with alcohol and drying at 100°, this was found to contain Cu = 42·69, agreeing approximately with $(C_7H_5O_3)_2Cu,3CuO$ (Calc., Cu = 44·12 per cent.), a basic salt, which has been obtained by other means (p. 189).

Thus, besides this and the first-mentioned basic salt of undetermined composition, there are four crystalline salicylates of copper, the anhydrous normal and acid salts, and two modifications of the tetrahydrate, these differing completely in colour and crystalline form.

Protocatechuate.—A red, insoluble salt, obtained by double decomposition in a very finely divided state. It was not analysed.

Gallate.—A red, insoluble salt, which, after drying at 100°, consisted of $(C_7H_5O_5)_2Cu,CuO$.

Tannate.—A pale brown, insoluble salt, which gave values indicating that it was a mixture of the normal and monobasic salts.

Quinate.—The salt formerly obtained (Trans., 1911, **99**, 178) by boiling quinic acid with copper carbonate was a green, crystalline, slightly soluble basic salt, $(C_7H_{11}O_6)_2Cu,CuO,8H_2O$; but if excess of acid is present, the solution on evaporation yields the normal salt in very light blue, wart-like masses of crystalline needles, which contain $2H_2O$ on drying at 100°, becoming anhydrous, and then decomposing, at 145°. The same salt may be precipitated by alcohol from an acid solution.

Phthalate.—The normal salt obtained by double decomposition is a light blue, almost insoluble compound, which becomes anhydrous very slowly at 100°. Hermann (*Annalen*, 1869, **151**, 78) obtained it in crystals with $1H_2O$, which it lost at 160°. A double salt, $(C_8H_4O_4)_2CuK_2$, and also a basic salt, have been mentioned as products of the action of potassium phthalate on copper acetate (Trans., 1911, **99**, 810), and a further investigation of the action has added a basic double phthalate to the list.

A solution of 60 grams of potassium phthalate in 100 c.c. was ground up with various quantities of copper acetate. The latter dissolved entirely when not more than one equivalent was used, forming a deep blue solution, which soon became almost solid through the formation of crystals of the double salt. The solubility of this salt in water is about 0·7 gram (=0·09 gram Cu) in 100 c.c., but it is insoluble in concentrated potassium phthalate solution. Solutions of it on evaporation and subsequent cooling generally yield a crop of the salt in large, rhombic crystals of a fine, full blue colour, although there is generally at first a separation of the mixed basic salts mentioned below. The crystals retain water at 100°, and become anhydrous at 155°. Four preparations of it gave closely concordant values, of which the mean was:

	Percentage.			Ratio.
	Cu.	K.	H_2O	Cu : K : H_2O
Found	12·60	15·55	6·23	1 : 2·01 : 1·74
Calculated	12·68	15·56	6·29	1 : 2·0 : 1·75

The proportion of water, as will be seen, necessitates the formula $4[(C_8H_4O_4)_2CuK_2],7H_2O$.

The basic salt mentioned above has every appearance of being a mixture of two substances of different intensities of blue, and analyses of it, as on previous occasions, gave values (Cu=33·96) intermediate between $(C_8H_4O_4)_2Cu,2CuO$ and $(C_8H_4O_4)_2Cu,3CuO$ (Cu=31·23 and 39·18 per cent. respectively). It is probably a mixture of these two.

The normal double salt when washed for some time on the filter changes somewhat suddenly to a very light blue, semicrystalline substance, and solutions of it when allowed to remain in the cold for some time give a more or less copious precipitate of the same substance. Analyses of different preparations of this precipitate after drying at 100°, and subsequent heating at 165°, gave:

	Percentage.			Ratio.
	Cu.	K.	H_2O.	Cu : K : H_2O.
I.	25·08	4·63	(4·95)	1 : 0·301 : (0·70)
II.	24·25	4·65	8·16	1 : 0·312 : 1·19
III.	23·88	4·45	9·57	1 : 0·296 : 1·41
Mean	24·40	4·58	8·87	1 : 0·303 : 1·30

The water eliminated at 165° varies somewhat, and in No. 1 the elimination was only partial; but the ratio Cu : K is fairly constant, and represents a substance of considerable complexity. The values on the anhydrous salt are Cu = 26·78 and K = 5·03, and it is impossible to accept it as a double salt, $(C_8H_4O_4)_7Cu_6K_2$, with the ratio Cu : K = 1 : 0·333, for such a salt would contain Cu = 23·72 and K = 4·86 per cent. Taking the ratio, as found, to be Cu : K = 10 : 3, the minimum molecular weight of the anhydrous salt will be 2354, which will not admit of the presence of more than ten phthalic nuclei, leaving an excess of base. The formula which this suggests is $(C_8H_4O_4)_{20}Cu_{17}K_6,3CuO$, with a molecular weight of 2 × 2417. The phthalates seem to be very complex, and their constitution requires further investigation.

Action of Potassium Hydroxide.

The potassium hydroxide solution used contained 0·035 gram per c.c.,* and phenolphthalein was used as indicator. Wherever the copper salt was sufficiently soluble, a solution of it was used; in other cases the solid salt was treated with the alkali in a mortar under continual grinding. It is difficult to ensure complete action in such cases, unless excess of alkali is present during part of the time, and as such excess tends to decompose any basic salt into hydroxide, the less soluble the copper salt is, the less exact are the values obtained. The solubilities are given in the second column of table I, in which the results with those salts which form no cupri-compounds are given. The proportion of potassium hydroxide required to produce an alkaline reaction is, of course, sufficient to determine the formula of the basic salt formed when none of the copper remains in solution. In no case was there any indication of different basic salts being formed in succession, as happens with copper sulphate under like conditions (Trans., 1907, **91**, 1982).

Of the nineteen salts examined, two are without action, and in four others either copper hydroxide, or a very highly basic salt of uncertain composition, is precipitated. The basic salts in the other thirteen cases form three groups: two have 1CuO, four have 3CuO, and seven have 7CuO, that is, the prevalent proportion of total copper in these salts, including the normal salt, is 1, 2, 4, or 8 atoms. What significance attaches to this fact is not clear.

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* The action of concentrated aqueous potassium hydroxide is not considered in the present communication; its action on all copper salts, organic or inorganic, results in some of the copper passing into solution at first, probably as a cuprite, and the subsequent decomposition of this into copper oxide, unless a cupri-compound is formed.

TABLE I.

Solubility, and Reaction of Copper Salts with Potassium Hydroxide.

Salt.	Solubility, grams Cu in 100 c.c.	Mols. KOH to precipitate each Cu.	Product.
Carbonate	0·00	no reaction	—
Oxalate	0·00	,, ,,	—
Acetate	2·30	[1·90	$(C_2H_3O_2)_2Cu,19CuO]$
Propionate	3·81	[1·95	$(C_3H_5O_2)_2Cu,39CuO]$
*iso*Butyrate	0·30	[1·97	Copper hydroxide]
Oleate	0·00	[2·12 *	,, ,,]
Butyrate	1·8	1·72	$(C_4H_7O_2)_2Cu,7CuO$
Valerate	0·012	1·77	$(C_5H_9O_2)_2Cu,7CuO$
*iso*Valerate	0·047	1·74	$(C_5H_9O_2)_2Cu,7CuO$
Succinate	0·012	1·77	$C_4H_4O_4Cu,7CuO$
Methylsuccinate	0·009	1·75	$C_5H_6O_4Cu,7CuO$
Maleate	0·017	1·74	$C_4H_2O_4Cu,7CuO$
Toluate	0·053	1·78	$(C_8H_7O_2)_2Cu,7CuO$
Formate	1·73	1·50	$(CHO_2)_2Cu,3CuO$
Fumarate	0·003	1·50	$C_4H_2O_4Cu,3CuO$
Aconitate	0·011	1·54	$(C_6H_3O_6)_2Cu_3,9CuO$
Benzoate	0·18	1·52	$(C_7H_5O_2)_2Cu,3CuO$
Cinnamate	0·003	(0·92 *)	$(C_9H_7O_2)_2Cu,CuO$
Phthalate	0·03	1·01	$C_8H_4O_4Cu,CuO$

* Uncertain. Some alcohol must be present for the alkali to react with the oleate.

Similar data respecting the salts which form cupri-compounds are given in table II.

TABLE II.

Solubility, and Reaction of Copper Salts with Potassium Hydroxide.

Copper partly precipitated.			None of the copper precipitated.		
Salt.	Solubitity, grams Cu in 100 c.c.	Mols. KOH.	Salt.	Solubility, grams Cu in 100 c.c.	Mols. KOH.
Glycollate	0·061	1·62	Tartrate	0·015	1·34
Lactate *	2·15	2·0	Saccharate	0·007	1·49
Citrate †	∝ ?	1·17—1·25	Mucate	0·000	1·59 ‖
Protocatechuate	0·000	(1·04)	Quinate ¶	0·02	0·67—1·0 ‖
Salicylate ‡	0·114	1·94	Glycerate	∝	1·02
Tannate §	0·000	(0·9)	Malate	∝	1·00
			Gallate ¶	0·000	1·6

* If the solution is concentrated, no precipitate.

† If the solution is dilute, no precipitate.

‡ A crystalline precipitate forms eventually.

§ Contained some basic salt.

‖ The solution soon gelatinises.

¶ A basic salt.

The glycollate, tartrate, saccharate, mucate and quinate have been dealt with in previous communications.

Glycerate.—The proportion of potassium hydroxide required to produce alkalinity is about 1KOH for every atom of copper, the whole of the copper remaining in solution whether there is much or little water present. On the addition of alcohol a light blue emulsion is precipitated, which, when dried in a vacuum and then at 100°, forms a dark blue, brittle solid. It begins to decompose at 135°. An analysis of it is given under *A*. On dissolving it in water and reprecipitating, only a small proportion is thrown down, and this (*B*) is much poorer in potassium than the first precipitate. The values are similar to those obtained in the case of the quinate, suggesting that potassium cupriglycerate, $C_2H_4(CuOH)O_2{\cdot}CO_2K$, is the first product, and that this, by the action of water, becomes converted into copper cupriglycerate:

	A.	Theory for potassium cupriglycerate.	*B.*	Theory for copper cupriglycerate.
Cu............	29·83	28·42	37·18	44·0
K	13·10	17·48	8·89	0·0

When excess of potassium hydroxide (2—3KOH) is added to copper glycerate, alcohol precipitates from the mixture a few drops of dark blue liquid, and causes a small, crystalline deposit to form on the sides of the vessel; but these products were not obtained in sufficient quantity for examination.

The crystalline compound obtained by the interaction of potassium glycerate on copper acetate, corresponding with the formula $(C_3H_5O_4)K(CuO)_4$ (Trans., 1911, **99**, 810), also requires further examination.

Malate.—Copper malate, either in dilute or concentrated solution, required almost exactly 1KOH to show alkalinity, no precipitation occurring. This indicates the formation of

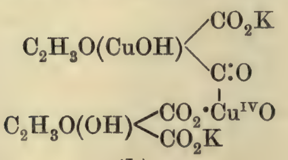
$$(C_4H_4O_5)_2CuK_2,CuO,$$

and on evaporation a viscid liquid was obtained, from which after a time dark blue, non-deliquescent, microscopic crystals separated; these, after dehydration at 160°, gave values agreeing with the above formula, the mean results from six different preparations being:

	Copper.	Potassium.	Ratio.
Found...............	26·12	16·76	2 : 21
Calculated	26·19	16·11	2 : 2

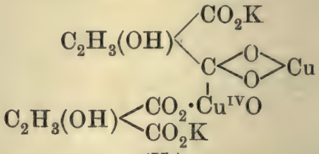
It was obtained in two different crystalline forms, one squat and rounded, these crystals being anhydrous, the other prismatic, containing approximately $2H_2O$. The addition of alcohol to the liquid precipitated this same substance as a viscid mass or very imperfect emulsion.

This substance is a further instance of the inacceptability of the view that in these cupri-compounds a copper atom displaces two hydrogen atoms of the alcoholic hydroxyls, for this would necessitate the substance after heating at 160° being still hydrated, thus, $C_4H_6CuO_2(CO_2)_4CuK_2,H_2O$, which is highly improbable; and that it can be regarded as a basic salt is scarcely possible, owing to its great solubility, its solution at 15° containing 50 grams per 100 c.c. That it contains copper in the alcoholic hydroxyl group, represented in formula (I) below, also seems improbable, as none of these compounds have been found to crystallise as this substance does, and such a formula does not agree with the analytical results, as it requires $Cu = 25{\cdot}26$ and $K = 15{\cdot}53$ per cent. It therefore would seem to be a compound with the formula (II), analogous to the



$$\begin{array}{l} C_2H_3O(CuOH)\langle\begin{array}{l}CO_2K\\ C{:}O\\ \;|\end{array}\\ C_2H_3O(OH)\langle\begin{array}{l}CO_2\cdot Cu^{IV}O\\ CO_2K\end{array}\end{array}$$

(I.)



$$\begin{array}{l} C_2H_3(OH)\langle\begin{array}{l}CO_2K\\ C\langle\begin{array}{l}O\\ O\end{array}\rangle Cu\\ \;|\end{array}\\ C_2H_3(OH)\langle\begin{array}{l}CO_2\cdot Cu^{IV}O\\ CO_2K\end{array}\end{array}$$

(II.)

cupricitrate No. 6 (Trans., 1910, **97**, 1846); and in further support of this view there is the fact that maleic acid (which contains no alcoholic hydroxyl) yields an excessively soluble compound with a precisely similar formula (p. 176).

Attempts to obtain other cuprimalates failed. The addition of excess of potassium hydroxide to copper malate precipitated a basic malate with, approximately, $5CuO$.

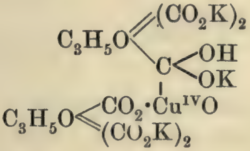
Citrate.—On adding potassium hydroxide to copper citrate in dilute solution, about $1{\cdot}17KOH$ for each atom of copper was required to produce alkalinity, and no precipitation occurred, either with this or a larger proportion of alkali. When there was only very little water present, $1{\cdot}25KOH$ was required, and about one-third of the copper was precipitated as a basic salt, insoluble in excess of alkali, and this, on drying, formed a brittle, olive-green substance, giving values on analysis agreeing exactly with $(C_6H_5O_7)_2Cu_3,6CuO$, or copper orthocitrate. It retained about $3H_2O$ at 100°, which it lost at 140°.

The copper which remained in solution was precipitated by alcohol as an imperfect emulsion or viscid mass, varying in composition in different experiments, and containing copper and potassium in the atomic ratios of 3 : 4 to 3 : 5.

When excess of alkali, 2 to 10 KOH, is added to copper citrate, and the liquid separated from the basic precipitate, and treated with alcohol, a very small crop of alkaline, viscid, rather large crystals is obtained. The most satisfactory preparation gave, after drying:

	At 100°.	At 130°.	Theory.
Cu	9·44 = 1·00	10·24	9·72
K	29·28 = 5·04	31·76	29·89
H_2O	7·82 = 2·92	—	—

these values agreeing with the cupricitrate No. 3 (Trans., 1910, **97**, 1842), which was not previously isolated with any certainty. As representing the first step in the formation of a cupricitrate by the action of potassium hydroxide, such a compound is of importance, the formula assigned to it being:



Unfortunately, in other cases it was only obtained contaminated with what was evidently potassium citrate precipitated by the alcohol.

Potassio-cupric citrate on treatment with potassium hydroxide requires exactly 1KOH for each atom of copper to produce alkalinity, indicating the formation of potassium citrate and the cupricitrate No. 6 (*loc. cit.*, p. 1846), according to the equation:

$$2KOH + 2[(C_6H_5O_7)_2CuK_4] = 2C_6H_5O_7K_3 + (C_6H_5O_7)_2K_4Cu,CuO.$$

Lactate.—No satisfactory results have so far been obtained with this salt. In weak solution (0·4 per cent. Cu) potassium hydroxide gave a precipitate when the proportion reached 1KOH, and alkalinity when it reached 2KOH. About 14 per cent. of the copper remained in solution, and the precipitate consisted of, approximately, $(C_3H_5O_3)_2Cu,5CuO$. From the liquid, alcohol caused the separation of a viscid mass, in which the proportion Cu : K = 1 : 1·4. If deficit of alkali had been added (1KOH), the precipitate by alcohol contained Cu : K = 1 : 0·76.

When solid copper lactate is treated with potassium hydroxide, the proportion required to dissolve it is 0·8KOH for each Cu. This solution, after twenty-four hours, deposits a copious precipitate of a basic salt approximating to $(C_3H_5O_3)_2Cu,CuO$.

Salicylate.—On the addition of an alcoholic solution of potassium hydroxide to the solid salt, the latter is transformed into a very light green, amorphous and anhydrous substance, stable up to 145°. Various preparations gave:

	Percentage.		Ratio.
	Cu.	K.	Cu : K.
I.	15·35	18·53	1 : 1·96
II.	15·11	18·59	1 : 1·96
III.	15·21	18·49	1 : 1·98
IV.	15·37	18·65	1 : 1·97
	15·26	18·56	1 : 1·97
Calc. for *A* ...	15·23	18·90	1 : 2
,, ,, *B* ...	14·72	18·11	1 : 2

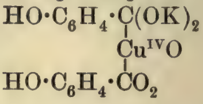
A.

Cu for H_2 in $(COH)_2$.

$$(C_6H_4O)_2Cu(CO_2K)_2$$

B.

A cupri-compound.



$$\begin{array}{l} HO\cdot C_6H_4\cdot C(OK)_2 \\ \qquad\qquad\quad | \\ \qquad\qquad\; Cu^{IV}O \\ \qquad\qquad\quad | \\ HO\cdot C_6H_4\cdot CO_2 \end{array}$$

The analyses agree with formula *A*; but on the addition of water, the substance gives a strong alkaline reaction, which is inconsistent with such a formula, and indicates a constitution represented by *B*. This is another instance, similar to that of the cupriglycollate and cupricitrate (Trans., 1911, **99**, 1350, 1351), wherein an alkaline cupri-compound, when anhydrous, appears to be a compound wherein the copper takes the place of hydrogen in alcoholic hydroxyl, and which can only be explained by a transformation of the one substance into the other. In the present instance both substances appear also to be capable of existing in solution, although in an unstable condition; thus, when aqueous, instead of alcoholic, potassium hydroxide (0·035 per cent.) is used, the copper salicylate dissolves completely to form a dark green *neutral* liquid, 1·94KOH (as a mean of four determinations) being required before the liquid becomes alkaline. In a few minutes a crystalline deposit begins to form, which soon becomes copious, and apparently consists of the same compound (which is alkaline) as that obtained when alcoholic potassium hydroxide is used, but in a hydrated condition (with $4H_2O$, which it loses at 145°), and slightly decomposed by the water present; in six different preparations the ratio Cu : K varied from 3 : 5 to 4 : 7. The decomposition occurring accounts for the alkali required to produce alkalinity, being only 1·94 instead of 2 KOH, as it should be according to the equations given below.

The salt prepared either by alcoholic or aqueous potassium hydroxide gives an alkaline reaction with water, a basic copper salicylate being gradually precipitated from the liquid; excess of water increases the amount of the precipitate eventually thrown down, 90 per cent. of the copper being precipitated when the tota copper present amounts to 0·01 gram per 100 c.c. For each atomi proportion of copper thus precipitated, half an atomic proportion of potassium (Found, 0·48) is liberated as alkali, and the precipitate has approximately the composition $(C_7H_5O_3)_2Cu,3CuO$, similar to the basic salicylate previously described,* so that the formation and decomposition of the cuprisalicylate will be represented by the equations:

$$(C_7H_5O_3)_2Cu + 2KOH = (C_7H_5O_3)_2(OK)_2CuO + H_2O.$$
$$(C_7H_5O_3)_2(OK)_2CuO + H_2O = (C_7H_5O_3)_2Cu,3CuO + 2KOH + 6C_7H_5O_3K.$$

From the neutrality of the solutions from which this substance separates, it would appear that $(C_7H_4O)_2Cu(CO_2K)_2$ must be capable of existing as such in solution, whilst, when it dissolves with excess of water to form an alkaline solution, the fact that the basic salt is only gradually precipitated indicates that the alkaline substance, or cupri-compound, must also be capable of existing temporarily in the dissolved condition. With the cupriglycollate and cupricitrate the alkaline compounds are quite stable in weak solution, but with the cupricitrate decomposition gradually occurs if the solution is strong.

The following salts, owing to their colour or indefiniteness in composition, did not appear suitable subjects for investigation:

Protocatechuate.—This on treatment with potassium hydroxide required 1·04KOH to produce alkalinity, about 50 per cent. of the copper passing into solution.

Gallate.—The basic copper gallate, $(C_7H_5O_5)_2Cu,CuO$, required about 1·6KOH for each atom of copper to produce alkalinity, and the whole of the copper passed into solution.

Tannate.—On treatment with potassium hydroxide, about 0·9KOH to each atom of copper was required to produce alkalinity, and about 10 per cent. of the copper passed into solution.

Sulphate Compounds.

The existence of a sulphate compound has been mentioned in the case of copper saccharate, and similar compounds probably exist in many other cases; that formed by copper malate has been investigated.

When fairly strong solutions of copper malate and copper sulphate are mixed, and either gently warmed or left in the cold, a copious precipitation of greenish-blue, well-crystallised solid gradually occurs. When heated at 100°, this turns to a full, rather dark blue, and suffers only a trifling further loss up to 140°, above which temperature decomposition begins. Five different preparations after drying at 140° gave, as a mean value:

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* Copper percentage found in the present case, 46·90, and in the former, 42·69; mean, 44·8; the above formula requiring 44·12. It contained $1H_2O$ at 100°, which it lost at 160°, remaining otherwise undecomposed at that temperature.

Cu = 39·01; SO_3 = 12·74. Ratio 4 : 1·04.
Calc., Cu = 40·34; SO_3 = 12·70. Ratio 4 : 1.

The analyses indicate a minimum molecular weight of 640, which is inconsistent with the presence of more than two malic acid groups, so that some of the copper must be present as CuO; the formula $(C_4H_4O_5Cu)_2,CuO,CuSO_4$ gives a molecular weight of 630, the percentage of copper and SO_3 in it being indicated by the values given above, and these agree fairly well with those found. What the constitution of the salt is can only be conjectured, but seeing that it contains excess of CuO, and yet is fairly soluble, it is probably a cupri-compound with $\dot{}Cu^{IV}SO_4$ entering into the molecule in a similar manner to that suggested for $\dot{}Cu^{IV}CO_3$ in the cupricarbonates (see Trans., 1911, **99**, 809).

The formation of a salt containing excess of cupric oxide from the neutral malate and sulphate involves the simultaneous formation of free acid, or of an acid salt, and the mixture, as a matter of fact, becomes strongly acid.

A solution of it on protracted boiling deposits an impure basic copper malate, and the addition of alcohol to a mixture of copper malate and sulphate precipitated a mixture of variable composition containing free malic acid.

The air-dried salt in four cases was found to contain H_2O = 27·72 (27·45 to 28·19), corresponding with $13·88H_2O$, and the dried salt on exposure to air re-absorbed this amount exactly. In two other cases the water present corresponded with only $8H_2O$, and this amount only was re-absorbed when the dehydrated salt was exposed to air, implying some difference between this and the other dehydrated specimens. The heat of dissolution of the two forms was determined, dissolving 4 grams in 600 c.c. of a 10 per cent. solution of hydrochloric acid, but the values obtained were 42·7 and 44·6 cal. per gram, respectively, and, as the difference between these values corresponded with only 0·007°, there was nothing to substantiate any difference in the nature of the substances.

Summary.

Copper salts of organic acids containing no alcoholic hydroxyl react with alkalis to form insoluble basic salts, whilst those of the oxy-acids form soluble cupri-compounds, with the copper in either the carboxylic or non-carboxylic portion of the molecule; in some cases a certain amount of basic salt is also formed. Cupri-salts of

monobasic acids, when the copper is in the non-carboxylic position, are, in nearly every case, very unstable.

Further evidence that copper in most cupri-salts is present as CuO, and not as copper displacing hydrogen, was obtained in several cases, especially in that of the salicylate and malate, the latter being of importance, because in the compound in question the copper must be in the carboxylic position, and former evidence applied chiefly to compounds with the copper in the non-carboxylic position.

In the case of copper glycerate a cupri-compound has been obtained differing in composition from the normal salt only by the elements of water, but certainly not being a hydrate. The two compounds have very different solubilities, colours, and temperatures of decomposition; and, in solution, the cupri-compound may easily be converted into the normal salt.

Similar modifications appear to exist in the case of basic copper citrate.

Two modifications of tetrahydrated copper salicylate were obtained, but there was nothing to suggest either of these being a cupri-compound. An alkaline potassium cuprisalicylate was obtained, which, like the corresponding cupriglycollate and cupricitrate, appears to change on dehydration into a neutral compound, the copper moving into the place of the hydrogen in the alcoholic hydroxyl.

Potassium cupri-compounds of malic and maleic acids were obtained, which might be represented as basic salts, but their great solubility shows that some other constitution must be assigned to them.

Amongst other compounds obtained, one which may be represented as consisting of basic copper malate with copper sulphate, is probably also a cupri-compound.

Thirteen basic salts, precipitated by alkali from salts of acids containing no alcoholic hydroxyl, conform to formulæ representing 1, 3, or 7 CuO united with a molecule of the normal salt. Besides these, the following compounds have been obtained:

Propionate.—A basic salt, $(C_3H_5O_2)_2Cu,CuO$, also with H_2O.

Methylsuccinate.—The normal salt; anhydrous. A double salt, $(C_5H_6O_4)_2CuK_2,3H_2O$.

Fumarate.—The normal salt; anhydrous, and as a dihydrate.

Maleate.—The normal salt; anhydrous, and as a monohydrate. An acid salt, $(C_4H_2O_4)_2CuH_2$, anhydrous, and with 4 and 8 H_2O. A cupri-compound, $(C_4H_2O_4)_2CuK_2CuO$.

Glycerate.—The normal anhydrous salt, and a salt corresponding with a monohydrate, but which is, apparently, a cupri-compound.

A basic salt, approximately $[(C_3H_5O_4)_2Cu]_3,CuO$. A potassium cupriglycerate, $C_2H_4(CuOH)O_2,CO_2K$.

Malate.—The normal salt in the anhydrous and monohydrated condition. A basic salt, $(C_4H_4O_5Cu)_4,CuO,6H_2O$, and another, approximately $C_4H_4O_5Cu,5CuO$. A cupri-salt,

$$(C_4H_4O_5)_2CuK_2Cu^{IV}O,$$

anhydrous and with $2H_2O$. A sulphate compound,

$$(C_4H_4O_5Cu)_2CuO,CuSO_4,$$

anhydrous and with 8 and 14 H_2O.

Aconitate.—The normal salt, anhydrous, and with 2 and 3 H_2O.

Citrate.—The normal salt, anhydrous, and with $2H_2O$. The basic salt, $(C_6H_5O_7)_2Cu_3,CuO$, anhydrous, and with 2 and 5 H_2O, one of these being probably a cupri-compound. A basic salt, or orthocupric citrate, $(C_6H_5O_7)_2Cu_3,6CuO,3H_2O$.

Lactate.—Two basic salts, approximately $(C_3H_5O_3)_2Cu,5CuO$ and $(C_3H_5O_3)_2Cu,CuO$.

Tannate.—The normal salt, anhydrous.

Salicylate.—The anhydrous normal salt, and two distinct modifications of a tetrahydrate of it. An acid salt,

$$(C_7H_5O_3)_2Cu,C_7H_5O_3H.$$

A basic salt, $(C_7H_5O_3)_2Cu,3CuO$. A potassium cuprisalicylate, $(C_6H_4O)_2Cu(CO_2K)_2$, anhydrous, and with $4H_2O$.

Gallate.—A basic salt, $(C_7H_5O_5)_2Cu,CuO$.

Phthalate.—The normal salt, and a double salt,

$$4[(C_8H_4O_4)_2CuK_2],7H_2O.$$

A mixture of basic salts, probably containing 2CuO and 3CuO. A double salt of basic character with the empyrical formula

$$(C_8H_4O_4)_{20}Cu_{17}K_3,3CuO.$$

HARPENDEN,
HERTS.

XXI.—*Molecular Rotatory Power in Normal Homologous Series. Part I. Optically Active Derivatives of the Higher Aliphatic Alcohols and Acids.*

By THOMAS PERCY HILDITCH.

THE values of a strictly additive physical property in successive members of a homologous series form an arithmetical progression the common difference of which represents the value of the property for the methylenic increment $\cdot CH_2\cdot$. Molecular mass is, however, the only physical characteristic which can be considered entirely additive; in all other cases the influences of chemical constitution are sufficiently strong to interfere with the simple additive rule.

Nevertheless, in certain cases (such as specific heat, capillarity, or refractivity) the additive influence is stronger than the constitutive, so that, at all events after the earlier members of a homologous series are passed, a definite increment is added to the molecular value of the property for each addition of a methylene group.

In other properties, the constitutive effects outbalance any additive influence, and as an example the case of molecular magnetic rotatory power may be cited. Sir W. H. Perkin (Trans., 1884, **45**, 574) showed that in this case each different homologous series possesses a characteristic "series constant" (which depends only on the chemical nature of the series in question), and, subsidiary to this, each methylene group present increases the molecular magnetic rotation by 1·023 units.

Finally, in still more constitutive properties (such as viscosity: compare Dunstan and Thole, *J. Chim. phys.*, 1909, **7**, 205; Getman, *Amer. Chem. J.*, 1908, **30**, 1077), the additive increment is almost or quite suppressed, and after the early members, the molecular value of the property becomes fairly constant for each member.

The extreme susceptibility of optical rotatory power (which, indeed, owes its existence to a specific type of constitution—molecular asymmetry) to the effects of chemical constitution has been frequently emphasised (compare Guye and Chavanne, *Bull. Soc. chim.*, 1896, [iii], **15**, 177; Frankland, Trans., 1903, **83**, 1342, etc.; Forster, *ibid.*, 1909, **95**, 942; Pickard and Kenyon, *ibid.*, 1911, **99**, 45, etc.), and it is of some interest to observe the change in molecular rotatory power on ascending homologous series.

Tschugaeff (*Ber.*, 1898, **31**, 360) drew attention to the fact that the molecular rotatory powers of the active amyl and menthyl esters of the normal fatty acids became constant after the first few members, but apparently did not extend his generalisation to other types of optically active compounds. He pointed out, however, that the optically active esters of acids isomeric with the normal aliphatic acids do not in general possess the same rotatory power.

Walden (*Ber.*, 1905, **38**, 355) tabulated the evidence then available, and concluded that Tschugaeff's rule held in many cases, but was not universal, whilst Miss Homfray and Guye (*J. Chim. phys.*, 1903, **1**, 505) regard it as a particular case of the more general rule that a change of mass at a point sufficiently distant from the asymmetric system produces little alteration in the rotatory power.

On the other hand, the author has remarked (Trans., 1908, **93**, 1; 1909, **95**, 1570) that changes in the rotatory power, due to alteration in constitution of part of the molecule, can be best appreciated with reference to the molecular rotatory power of the nearest normal aliphatic derivative, and has suggested that the difference between these two values may be interpreted as a rough indication of the "anomaly" in optical activity introduced by the constitutive change.

The possibility of using such a "series constant" for optical activity has rendered desirable a more thorough revision of the data on which the Tschugaeff rule is based. A somewhat exhaustive survey of the existing data shows that some forty series of optically active homologous compounds have been described, but in about half the cases the members dealt with are only the first three, which renders them of little use for the present purpose.

In the remaining groups, many reach a constant molecular rotatory power almost at once, others after several members, and others, again, show no sign of attaining a constant value within the limits so far investigated. A few examples of each class may be given.

I.—*Series in which Approximate Constancy of* $[M]_D$ *is Rapidly Attained.*

(*a*) *Esters of Optically Active Alcohols.*

Acid.	Amyl.[1]	Bornyl.[2]
Formic	+2·3°	−89·2°
Acetic	3·3	89·2
Propionic	4·0	89·9
n-Butyric	4·3	89·6
n-Valeric	+4·3°	−89·0°
n-Hexoic	4·5	—
n-Heptoic	4·4	—
n-Octoic	4·5	—
n-Nonoic	4·5	—

[1] Guye and Chavanne, *Bull. Soc. chim.*, 1896, [iii], **15**, 177 (amyl alcohol, $[\alpha]_D$ −4·5°).

[2] Minguin and Bollemont, *Compt. rend.*, 1902, **134**, 608.

(*b*) *Salts of Brucine and Cinchonine*[1] (compare p. 200).

(*c*) *Alkyl Derivatives of Ricinoleic Acid*[2] *and of Bornylamine.*[3]

(*d*) *Acyl Derivatives of Bornylamine*[4] *and Menthylamine,*[5] *and of Ethyl Malate.*[6]

[1] Hilditch, Trans., 1909, **95**, 1570.

[2] Walden, *Ber.*, 1903, **36**, 781.

[3] Forster, Trans., 1899, **75**, 934 (in alcohol).

[4] Frankland and Barrow, *ibid.*, 1909, **95**, 2017.

[5] Birz, *Zeitsch. physikal. Chem.*, 1893, **12**, 723.

[6] Reitter, *ibid.*, 1901, **36**, 129.

II.—*Series in which Approximate Constancy of* $[M]_D$ *is only attained after several members.*

(*a*) *Alkyl Derivatives of Tartramide and Malamide.*

Alcohol.	Tartaric diamides.[7]	Malic diamides.[8]	Alcohol.	Tartaric diamides.[7]	Malic diamides.[8]
Dimethyl......	+262°	+109·6°	Di-*n*-butyl	+291°	+116·5°
Diethyl	282	111·8	Di-*n*-heptyl	303	118·4
Di-*n*-propyl...	290	114·7			

[7] Frankland and Twiss, Trans., 1906, **89**, 1852.

[8] Frankland and Done, *ibid.*, 1906, **89**, 1859.

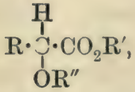
(*b*) *Normal Aliphatic Esters of Glyceric*[9] *and Diacetylglyceric Acids,*[9] *and of Monomethoxy- and Monoethoxy-succinic Acids.*[10]

III.—*Series in which Constancy of* $[M]_D$ *is not reached.*

(*a*) *Esters of Diacyltartaric Acids.*[11]

	Dimethyl.	Diethyl.	Di-*n*-propyl.	Di-*n*-butyl.
Diacetyltartrate	—	+14·5°	+42·6°	+27·7°
Dipropionyltartrate	−31·0°	+ 1·6	+19·4	+25·8
Di-*n*-butyryltartrate	−48·0	− 2·8	+19·5	+24·1
Di-*n*-valeryltartrate	−55·7	− 7·9	+13·2	+20·6
Di-*n*-hexoyltartrate	−59·5	−12·6	+ 9·5	—

It is at once noticeable that all the series included in tables II and III (glycerates, malates, and tartrates) contain the asymmetric system:



$$R\cdot\overset{\displaystyle H}{\underset{\displaystyle OR''}{C}}\cdot CO_2R',$$

and that in the tartrates (which are least of all in accord with the Tschugaeff rule) this system, which possesses the two unsaturated groups $\cdot CO_2R'$ and $\cdot OR''$ adjacent to the asymmetric carbon atom, is repeated symmetrically about the centre of the molecule.

The author has previously shown (Trans., 1909, **95**, 331, 1570; *Zeitsch. physikal. Chem.*, 1911, **77**, 482) that unsaturation, and especially symmetrically conjugated unsaturation, of this type leads to anomalous values of optical rotatory power, and therefore it appears very possible that the inconstant nature of the molecular rotatory power in the above-mentioned cases is caused by the disturbing influence of the unsaturated radicles directly united to the asymmetric atoms. This suggestion is supported by the series quoted in table II, inasmuch as the latter reach tolerable constancy after the first half-dozen or so members are passed.

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[9] Frankland and McGregor, Trans., 1893, **63**, 511, 1410, 1419; 1894, **65**, 750.

[10] Purdie and co-workers, *ibid.*, 1893, **63**, 217, 229; 1895, **67**, 944, 957.

[11] Freundler, *Bull. Soc. chim.*, 1894, [iii], **11**, 305.

It is therefore intended to examine a number of derivatives of the tartrates, malates, etc., of very high molecular weights (such as cetyl esters, stearyl and palmityl derivatives, etc.) in order to test whether the suggested disturbing influences of unsaturation are overcome on ascending the various homologous series to a sufficient distance.

It appeared desirable, however, in the first place, to ensure that series of the normal type quoted in table I maintained their constant molecular rotatory power equally high in their respective groups, and this communication includes a description of this preliminary work, which, it may be said at the outset, confirms Tschugaeff's rule in these cases.

Before quoting the figures obtained in this investigation, it will be well to draw attention to the following points:

(*a*) The most appropriate constant for the quantitative study of optical activity.

(*b*) The comparability of different series when the latter contain varying numbers of asymmetric carbon atoms.

(*a*) *Specific rotatory power* $[\alpha]_D$ affords a comparison of equal masses of active substance, and whilst beyond this it possesses no precise physical meaning or substantiation, it is the only fundamental constant of optical activity which we at present possess. Of the two derived constants, *molecular rotatory power* $[M]_D$ and *molecular deviation* $[\delta]_D$ (Guye, *Compt. rend.*, 1893, **116**, 1451), the latter has found little application; Tschugaeff (*loc. cit.*) pointed out that specific rotatory power has little meaning with respect to either the molecular hypothesis or from a stereochemical point of view, whereas molecular rotatory power gives a direct comparison of the rotation produced by the active molecules.

Although, as Forster (*Trans.*, 1909, **95**, 942) has emphasised, there may be no absolute physical proof of the validity of the expression $[\alpha]_D$, it is the only one available, and it has stood the test of a century's practical use; and, for the same reasons as those given by Tschugaeff, it will be employed in the present investigation in its derived form of molecular rotatory power.

(*b*) Doubt has frequently been expressed (compare, for example, Pickard and Kenyon, *loc. cit.*) as to the possibility of comparing the results from series derived from different optically active substances containing varying numbers of asymmetric atoms (for example, amyl alcohol and menthol), and furthermore, in the case of substances containing more than one asymmetric atom, as to whether each asymmetric atom will be affected similarly by a given change of constitution, since the different atoms will be at varying distances from the group which has suffered alteration.

With regard to the second point, there is no direct evidence, so far as the author is aware, that the optical activity of a polyasymmetric grouping is derived in any way additively from the activity of each asymmetric atom. Indeed, it would appear more probable that, although such atoms doubtless act each as a centre of asymmetry, the resultant rotation is due, as Pasteur (*Compt. rend.*, 1852, **35**, 180) originally suggested, to *molecular*, and not *atomic*, asymmetry. Two facts which seem to favour this distinction are (i) the absence of any simple relation between the rotation of a compound possessing *n*, and a nearly-related compound possessing $n-1$, asymmetric atoms (for example, *l*-menthol and *l*-menthone), and the absolute dissimilarity of the rotatory powers of isomerides possessing similar asymmetric systems (for example, menthol and borneol); and (ii) the well-established circumstance (Perkin, Pope, and Wallach, Trans., 1909, **95**, 1789; Mills and Miss Bain, *ibid.*, 1910, **97**, 1866) that a compound may exhibit optical activity, owing to molecular asymmetry, in the absence of any asymmetric carbon atom at all.

Hence it appears to the author that the number of asymmetric atoms present in a given molecule has little bearing, according to the evidence at present existing, upon the changes induced in the rotatory power by constitutive influences, providing, of course, that no centres of asymmetry are destroyed or created by the alteration in chemical constitution.

With reference to the former question of drawing generalisations from series derived from varying asymmetric systems, it must be admitted that the existing results tend to show the validity of the comparison. For example, the following homologous series (table I, grouped according to the number of "asymmetric atoms" present) conform strictly to the Tschugaeff rule:

1 *asymmetric atom.*—Amyl esters, ricinoleic esters, acyl derivatives of ethyl malate.
3 *asymmetric atoms.*—Bornyl and menthyl esters, alkyl bornylamines, acyl bornylamines, and menthylamines.
4 *asymmetric atoms.*—Cinchonine salts.
Unknown number of asymmetric atoms.—Brucine salts.

Moreover, apart from derivatives of the above types (esters and salts), in which the change in constitution takes place at a point relatively distant from the centres of asymmetry, series in which the increasing alkyl radicles are directly attached to an asymmetric atom show an exactly parallel behaviour. Two examples may be cited, in one of which there is but little unsaturation (methyl-*n*-alkylcarbinols, Pickard and Kenyon, *loc. cit.*), whilst in the second (alkylated malic acids, Purdie and co-workers, *loc. cit.*), unsaturation and asymmetry of the $R\cdot CH(OH)\cdot CO_2H$ type (compare p. 195) is present. The first conforms to the constant molecular rotatory power rule almost at once, the second (of which only the first three members are available) does not reach a constant value for $[M]_D$.

Constancy of molecular rotatory power is thus a well-defined characteristic of many optically active homologous series, simple or complex, and comprising asymmetric systems with one, three, four, or more atomic centres of asymmetry.

The compounds the optical activity of which is about to be described include the higher aliphatic esters or salts of menthol, camphoric acid, camphor-β-sulphonic acid, brucine, and cinchonine.

The polarimetric measurements were made at 20° in a 2-dcm. tube in chloroform solution at two concentrations (5·0 and 2·5 per cent.), and, also, in the case of menthyl esters, in alcohol solution at the same concentrations. As usual, the alkaloid salts were made up from the requisite amounts of base and acid (accurately weighed), and subsequently recovered for characterisation. The optically active materials from which the various derivatives were prepared possessed the following rotations at 20°:

	Solvent.	Concentration per cent.	α_D.	$[\alpha]_D$.
Menthol	Chloroform.	5·0	−4·891°	− 48·91°
Brucine	,,	2·5	−6·049	−120·98
Cinchonine	Alcohol	0·5	+2·245	+224·5
Camphoric acid	,,	5·0	+4·867	+48·67
Camphor-β-sulphonic acid ...	Chloroform.	5·0	+3·947	+39·47
,, ,, ,, ...	Water	5·0	+2·395	+23·95
Camphor-β-sulphonyl chloride	Chloroform.	5·0	+3·201	+32·01

The following tables comprise the result of the polarimetric determinations:

I.—*Menthyl Esters.*

(*a*) *In Chloroform.*

	5·0 per cent.			2·5 per cent.		
	α_D.	$[\alpha]_D$.	$[M]_D$.	α_D.	$[\alpha]_D$.	$[M]_D$.
Menthyl myristate...	−4·283°	−42·83°	−156·7°	−2·137°	−42·74°	−156·4°
Menthyl palmitate	3·979	39·79	156·8	1·967	39·34	155·0
Menthyl stearate ...	3·671	36·71	154·9	1·847	36·94	155·9

(*b*) *In Alcohol.*

	5·0 per cent.			2·5 per cent.		
	α_D.	$[\alpha]_D$.	$[M]_D$.	α_D.	$[\alpha]_D$.	$[M]_D$.
Menthyl myristate ...	−4·341°	−43·41°	−158·9°	−2·193°	−43·86°	−160·5°
Menthyl palmitate...	4·017	40·17	158·2	2·027	40·54	159·7
Menthyl stearate ...	3·773	37·73	159·2	1·885	37·70	159·1

II.—*Brucine Salts.*

	5·0 per cent.			2·5 per cent.		
	α_D.	$[\alpha]_D$.	$[M]_D$.	α_D.	$[\alpha]_D$.	$[M]_D$.
Brucine myristate ...	−3·967°	−39·67	−246·8°	−1·983°	−39·66°	−246·7°
Brucine palmitate ...	3·807	38·07	247·5	1·911	38·22	248·4
Brucine stearate	3·648	36·48	247·4	1·827	36·54	247·7

III.—*Cinchonine Salts.*

	5·0 per cent.			2·5 per cent.		
	α_D.	$[\alpha]_D$.	$[M]_D$.	α_D.	$[\alpha]_D$.	$[M]_D$.
Cinchonine myristate	+13·353°	−133·53°	+697·1°	+6·709°	+134·18°	+700·3
Cinchonine palmitate	12·779	127·79	703·1	6·317	126·34	695·0
Cinchonine stearate	12·221	122·27	706·6	6·071	121·42	702·5

IV.—*Alkyl Hydrogen Camphorates.*

	5·0 per cent.			2·5 per cent.		
	α_D.	$[\alpha]_D$.	$[M]_D$.	α_D.	$[\alpha]_D$.	$[M]_D$.
Cetyl hydrogen camphorate..............	+2·043°	+20·43°	+86·6°	+1·021°	+20·42°	+86·6°
Myricyl hydrogen camphorate	1·429	14·29	88·6	0·729	14·58	90·4°

V.—*Alkyl Camphor-β-sulphonates.*

	5·0 per cent.			2·5 per cent.		
	α_D.	$[\alpha]_D$.	$[M]_D$.	α_D.	$[\alpha]_D$.	$[M]_D$.
Cetyl camphor-β-sulphonate	+2·193°	+21·93°	+100·0°	+1·087°	+21·74°	+99·2°
Myricyl camphor-β-sulphonate...........	—	—	—	0·765	15·30	99·5

In the concluding table are collected the molecular rotatory powers of the complete series of these esters and salts; the values for the lower members are taken from the author's measurements (Trans., 1909, **95**, 331, 1570), with the exception of the alcohol solutions of menthyl acetate to *n*-hexoate (Rupe, *Annalen*, 1903, **327**, 157):

I.—*Esters and Salts of* n-*Aliphatic Acids.*

	Menthyl (chloroform).		Menthyl (alcohol.)	
Concentration: per cent.	5·0.	2·5.	5·0.	2·5.
Acetate	−158·2°	−157·0°	−149·9°	—
Propionate..............	156·6	157·2	162·2	—
n-Butyrate..............	161·2	161·7	164·7	—
n-Valerate..............	161·9	162·1	165·7	—
n-Hexoate..............	164·4	168·1	164·7	—
n-Heptoate	—	—	165·9	—
n-Myristate	156·7	156·4	158·9	160·5°
Palmitate	156·8	155·0	158·2	159·7
Stearate	154·9	155·9	159·2	159·1

I.—*Esters and Salts of* n-*Aliphatic Acids* (*continued*).

	Brucine.		Cinchonine.	
Concentration : per cent.	5·0.	2·5.	5·0.	2·5.
Acetate	−258·0°	−260·6°	+691·9°	+706·7°
Propionate	248·1	252·3	690·7	707·9
n-Butyrate	247·4	251·2	692·6	714·1
n-Valerate	247·4	251·6	692·8	704·1
n-Hexoate	246·8	252·8	672·7	698·6
n-Heptoate	—	—	—	—
n-Myristate	246·8	246·7	697·1	700·3
Palmitate	247·5	248·4	703·1	695·0
Stearate	247·4	247·7	706·6	702·5

II.—*Esters of Optically Active Acids.*

	Hydrogen camphorates.		Camphor-β-sulphonates.	
Concentration : per cent.	5·0.	2·5.	5·0.	2·5.
Methyl	+123·5°	+125·2°	+107·3°	+106·8°
Ethyl	88·3	90·7	114·2	112·6
n-Propyl	93·8	93·3	—	—
n-Butyl	91·1	92·8	—	—
Cetyl	86·6	86·6	100·0	99·2
Myricyl	88·6	90·4	—	99·5

The approximate constancy is well maintained throughout, although there may possibly be a very slight diminution in the value of the constant after a certain point on passing up the series; it is also noticeable that the effect of concentration on the rotations of the alkaloid salts diminishes on ascending the series.

It is hoped to continue this line of research, both in the direction of the rotatory powers of the higher homologous derivatives of more unsaturated acids, and of the examination of certain substituted series of the higher fatty acids, such as the bromo- and hydroxy-derivatives.

EXPERIMENTAL.

The *menthyl* esters were prepared by warming the acids with a very slight excess of pure thionyl chloride for about twenty minutes, the excess being then removed by warming to 100° under diminished pressure; the theoretical quantity of menthol was then added, and the mixture heated at 100° under diminished pressure for two hours. The product was dissolved in chloroform, and extracted two or three times with aqueous potassium carbonate. The chloroform layer was finally separated, dried, and evaporated, and on boiling the residue with alcohol and setting aside for some time the ester slowly crystallised out, and was purified from a little hot alcohol. The table illustrates the properties and analyses of the esters used:

			Analysis.			Found.			Theory.	
		M. P.	Subst.	CO_2.	H_2O.	C%.	H%.	Formula.	C%.	H%.
Myristate...	Thin, colourless prisms.	32°	0 0994	0·2858	0·1181	78·41	13·20	$C_{24}H_{46}O_2$	78·68	12·57
Palmitate..	Large, thin prisms.	36	0·1756	0·5082	0·2082	78·93	13·05	$C_{26}H_{50}O_2$	79·20	12·69
Stearate	Small, colourless tablets.	39	0·1191	0·3459	0·1346	79·26	12·49	$C_{28}H_{54}O_2$	79·62	12·80

The characteristics of the *brucine* and *cinchonine* salts examined are given below:

Brucine myristate	$C_{37}H_{54}O_6N_2,\frac{1}{2}H_2O$	Cream, wax-like crystals, melting a 60—65°, and frothing at 125°.
Brucine palmitate	$C_{39}H_{58}O_6N_2,2H_2O$	Soft, white, microcrystalline powder, which melts to a clear liquid at 70°, and froths at 100—105°.
Brucine stearate	$C_{41}H_{62}O_6N_2,1\frac{1}{2}H_2O$	White, crystalline powder, melting at 70—72° to a clear liquid, which froths at 110—115°.
Cinchonine myristate ...	$C_{33}H_{50}O_3N_2$	Tough, waxy crystals, melting and decomposing at 215°.
Cinchonine palmitate ...	$C_{35}H_{54}O_3N_2$	Soft, white, crystalline powder, which melted and commenced to blacken at 230°.
Cinchonine stearate......	$C_{37}H_{58}O_3N_2$	Small, slender, white prisms, melting and decomposing at 248°.

The following analyses of these salts were made:

				Found.		Calc.	
	Subst.	CO_2.	H_2O.	C%.	H%.	C%.	H%.
Brucine myristate	0·1800	0·4640	0·1461	70·26	9·02	70·37	8·72($\frac{1}{2}H_2O$)
Brucine palmitate	0·1284	0·3211	0·1069	68·19	9·25	68·22	9·04($2H_2O$)
Brucine stearate.........	0·1500	0·3855	0·1281	70·08	9·49	69·79	9·22($1\frac{1}{2}H_2O$)
Cinchonine myristate...	0·1001	0·2784	0·0847	75·84	9·40	75·86	9·57
Cinchonine palmitate ..	0·1414	0·3963	0·1296	76·40	10·18	76·35	9·82
Cinchonine stearate	0·1013	0·2848	0·0940	76·68	10·31	76 83	10·03

Cetyl and *myricyl hydrogen camphorates* were obtained when equivalent amounts of camphoric anhydride and the alcohol were heated at 170° for eight hours in an oil-bath; the cooled product was dissolved in a considerable quantity of ether, and extracted twice with dilute aqueous potassium carbonate. The aqueous layer was separated and acidified with dilute sulphuric acid, and again extracted with ether. The ethereal extract, after being dried and the ether evaporated, was crystallised two or three times from chloroform.

Cetyl hydrogen camphorate	$C_{26}H_{48}O_4$	White, waxy nodules, which melted at 35°.
Myricyl hydrogen camphorate...	$C_{40}H_{76}O_4$	Wax-like, crystalline powder, melting at 71—72°.

Analyses:

				Found.		Calc.	
	Subst.	CO_2.	H_2O.	C%.	H%.	C%.	H%.
Cetyl ester	0·0921	0·2474	0·0981	73·24	11·84	73·58	11·32
Myricyl ester	0·0975	0·2781	0·1058	77·78	12·06	77·41	12·26

Cetyl camphor-β-sulphonate, $C_{26}H_{48}O_4S_2$, resulted when the alcohol was heated with a large excess of camphor-β-sulphonyl chloride in 50 per cent. aqueous pyridine at 100° for two hours.

Some cetyl alcohol still remained unattacked, but several recrystallistions from hot alcohol gave a sample of the pure sulphonic ester, melting at 52°.

Myricyl camphor-β-sulphonate, $C_{40}H_{76}O_4S$, was produced in good yield by heating the alcohol with excess of the sulphonyl chloride in pyridine at 100° for some hours. After several recrystallisations from ether, it melted at 78°.

Analyses:

				Found.		Calc.	
	Subst.	CO_2.	H_2O.	C%.	H%.	C%.	H%.
Cetyl ester	0·0929	0·2336	0·0955	68·58	11·42	68·42	10·52
Myricyl ester	0·1086	0·2968	0·1129	74·52	11·57	73·62	11·45

The author desires to acknowledge the kindness of Professor Collie, in whose laboratory this investigation was carried out.

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XXII.—*Molecular Rotatory Power in Normal Homologous Series. Part. II. The Menthyl Esters of the α-Bromo-aliphatic Acids.*

By HAROLD CHRISTOPHER and THOMAS PERCY HILDITCH.

THE existence of "series constants" in the molecular rotatory powers of optically active esters or salts of normal homologous saturated aliphatic acids or alcohols has been recently discussed by one of us (Part I, this vol., p. 192), and it has been concluded that such constancy occurs with regularity in those series in which only one centre of unsaturation (the carboxylic residue uniting the alcohol, or base, with the acid) is present. On the other hand, in cases where a number of unsaturated groups occur in close proximity to the optically active nucleus, a constant value of the molecular rotatory power is not noticeable, at all events in the earlier members of those series which have hitherto been investigated. The examination of compounds of high molecular weight in these respective series is now being undertaken, and in the meantime it is of some interest to study the effect of introducing an unsaturated group, in close proximity to the carboxyl residue, in series which, when completely saturated, accord well with the rule of constant molecular rotatory power first indicated by Tschugaeff (*Ber.*, 1898, **31**, 360).

From a somewhat different point of view, it may be pointed out that whilst the earlier members of a saturated optically active homologous series possess rotatory powers somewhat below the mean normal value subsequently attained, the reverse appears to hold when a substituent possessing residual affinity is attached to the carbon atom adjacent to the carboxyl group; in other words, the optical activity is enhanced in virtue of the presence of the second unsaturated group. The following data illustrate this statement:

(*a*) *Menthyl Esters.*

	$[M]_D$.	$[D]_D$.*
Mean normal value (propionate to *n*-valerate) † ...	−159·5°	—
Menthyl formate ‡	−146·3	−13·2°
Menthyl acetate †	−157·0	+ 2·8
Menthyl bromoacetate §	−168·8	+ 9·3
Menthyl α-bromopropionate ‖	−158·4	− 1·1
Menthyl chloroacetate §	−171·2	+11·7
Menthyl α-chloropropionate ‖	−155·2	− 4·3
Menthyl phenylacetate ¶	−185·2	+25·7
Menthyl α-phenylpropionate ¶	−178·4	+18·9

(*b*) *Brucine Salts.*

	$[M]_D$.	$[D]_D$.*
Mean normal value (propionate to *n*-hexoate) † ...	−247·4°	—
Brucine acetate †	−258·0	−10·6°
Brucine phenylacetate **	−161·7	+85·7

* It must be borne in mind that the sign of the "anomaly" $[D]_D$ is based on the relation of the normal value to the molecular rotatory power of the parent alcohol or base (for example, menthol, $[M]_D - 76·3°$; brucine, $[M]_D - 476·7°$).

† Hilditch, Trans., 1909, **95**, 1570.

‡ Tschugaeff, *loc. cit.*

§ Tschugaeff, *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 606.

‖ Cohen, Trans., 1911, **99**, 1058.

¶ Rupe, *Annalen*, 1909, **369**, 311.

** Hilditch, Trans., 1908, **93**, 1388.

We have therefore prepared a number of menthyl esters of the α-bromo-aliphatic acids (from bromoacetic to α-bromopalmitic) in order to correlate the behaviour of this unsaturated type of homologous series with that of the saturated compounds, and in the hope of throwing some light on the anomalous nature of the cases referred to above, in which no constant value of molecular rotatory power has yet been observed.

We have chosen for our purpose the α-bromo-derivatives, for the reason that, although bromine does not influence rotatory power to the same extent as more distinctively unsaturated groups (such as phenyl, $C_6H_5\cdot$, or ethylene, $\cdot CH{:}CH\cdot$), the higher compounds in this series are the most readily obtained in a state of purity (by means of the reaction of Hell, Volhard, and Zelinsky, *Ber.*, 1881, **41**, 891; *Annalen*, 1887, **242**, 144). It may be noted in passing that no evidence of any "asymmetric synthesis" was observed in esterifying these acids with menthol, although all of them, except bromoacetic acid, contain an asymmetric carbon atom. The presence of this configuration therefore, in view of our unsuccessful attempts to detect any signs of resolution into the active forms, cannot be held to influence the nature of the observed rotatory powers.

It might be predicted from the relative molecular rotatory powers of menthyl bromoacetate and α-bromopropionate that, just as in the simple aliphatic acids the values rapidly *rise* to an approximately constant figure, so in the substituted series the positive anomaly would *fall*, and a constant molecular rotatory power again be attained. This is supported, indeed, by the experimental data we have obtained, but the latter do not, unfortunately, permit us at present to state with confidence whether this constant value is approximately the same as that for the saturated compounds, or whether each substituted homologous series possesses a characteristic and independent constant molecular rotatory power, due to the effect of the substituting radicle. We hope to undertake further experiments to elucidate this point, and thus to determine whether the presence of a given substituent tends when sufficiently high members of each series are considered to the existence of some sort of definite "replacement value" in each particular case, by comparison with the saturated normal series.

The polarimetric measurements were performed in dry chloroform solution at concentrations of 5·0 and 2·5 per cent.; the menthol used in the preparation of the esters had, in 5 per cent. chloroform solution in a 2-dcm. tube, $\alpha_D - 4{\cdot}891°$, whence $[\alpha]_D\ -48{\cdot}91°$.

All readings were taken in a 2-dcm. tube at 20°. The results were as follows:

	5·0 per cent.			
	α_D.	$[\alpha]_D$.	$[M]_D$.	$[D]_D$.
Menthyl bromoacetate	−6·264°	−62·64°	−173·6°	+14·1°
Menthyl α-bromopropionate...	5·705	57·05	166·1	6·6
Menthyl α-bromobutyrate ...	5·349	53·49	163·1	3·6
Menthyl α-bromovalerate ...	5·137	51·37	163·9	4·4
Menthyl α-bromohexoate	4·849	48·49	161·4	1·9
Menthyl α-bromomyristate ...	—	—	—	—
Menthyl α-bromopalmitate ...	3·434	34·34	162·5	3·0

	2·5 per cent.			
	α_D.	$[\alpha]_D$.	$[M]_D$.	$[D]_D$.
Menthyl bromoacetate	−3·160°	−63·20°	−175·1°	+15·6°
Menthyl α-bromopropionate...	2·857	57·14	166·3	6·8
Menthyl α-bromobutyrate ...	2·679	53·58	163·4	3·9
Menthyl α-bromovalerate	2·573	51·46	164·3	4·8
Menthyl α-bromohexoate	2·403	48·06	160·0	0·5
Menthyl α-bromomyristate ...	1·822	36·44	162·2	2·7
Menthyl α-bromopalmitate ...	1·699	33·98	160·8	1·3

It is interesting to compare the rotatory powers of the corresponding individual non-substituted and bromo-esters, in addition to the respective "anomalies" of the latter compounds; it will be noticed at once that the latter values, which are derived from the mean molecular rotatory power of the saturated series, rapidly become of an insignificant order of magnitude as soon as the first two members are passed.

The next table affords a comparison between the molecular rotatory powers of each specific pair of esters; the figures for the normal esters are taken from previous papers (*loc. cit.*).

	5 per cent.		2·5 per cent.	
Menthyl.	$[M]_D$.	Diff.	$[M]_D$.	Diff.
Acetate	−158·2°	—	−157·0°	—
Bromoacetate	173·6	+15·4°	175·1	+18·1°
Propionate	156·6	—	157·2	—
α-Bromopropionate...	166·1	+ 9·5	166·3	+ 9·1
n-Butyrate	161·2	—	161·7	—
α-Bromobutyrate......	163·1	+ 1·9	163·4	+ 1·7
n-Valerate	161·9	—	162·1	—
α-Bromovalerate	163·9	+ 2·0	164·3	+ 2·1
n-Hexoate	164·4	—	168·1	—
α-Bromohexoate	161·4	− 3·0	160·0	+ 8·1
Myristate	156·7	—	156·4	—
α-Bromomyristate ...	—	—	162·2	+ 5·8
Palmitate	156·8	—	155·0	—
α-Bromopalmitate ...	162·5	+ 5·7	160·8	+ 5·8

This table brings out the following points:

(*a*) In the lowest members, the enhancing effect of the unsaturated substituent on the optical activity is well marked.

(*b*) In the succeeding members the rotations are almost identical, and, in one case, the bromo-ester possesses a smaller rotatory power than the saturated compound.

(*c*) In the higher members, a constant difference in molecular rotatory power is exhibited between corresponding members of the two series.

We are therefore enabled to draw the following conclusions from our results:

(*a*) The enhancing effect of unsaturation is most clearly displayed in the lower members of the series.

(*b*) It appears very possible that the tendency to sub-normal values in the lower members of a series (due to some at present unknown cause) exists also in series containing unsaturated groups, and indeed persists longer in the latter class of compounds. Accordingly, although the effect of residual affinity overbalances that now under consideration in the first few members, the latter conflicting effect, being more prolonged, produces in the ensuing compounds the same phenomenon of a molecular rotatory power less than that characteristic of the higher members of the series. The net result is to produce a rapid diminution of rotatory power to a minimum, followed by a much smaller rise to an approximately constant value.

(*c*) The differences between the corresponding myristic and palmitic esters are strikingly suggestive of the presence of a definite increment in molecular rotatory power accompanying the replacement of hydrogen by bromine in sufficiently high members of the homologous series.

Nevertheless, in view of the small numerical difference (amounting only to six units of molecular rotation, or between 3 to 4 per cent. of the individual rotatory powers), and in the absence of data from similar series which could afford confirmatory evidence on the subject, we do not feel justified at present in definitely affirming the existence of constant "replacement values" of the nature explained above.

(*d*) Our results prove that in homologous series containing groups which possess residual affinity, the presence of unsaturation introduces a disturbing influence which causes the ultimate attainment of constant molecular rotatory power to be notably hindered.

EXPERIMENTAL.

The first three esters in the series (the bromoacetate, α-bromopropionate, and α-bromobutyrate) were obtained by dissolving the bromide of the respective bromo-acids in chloroform, and adding the equivalent quantity of menthol. The mixture was warmed, at first gently, and subsequently heated under a reflux condenser for an hour. The chloroform was then distilled off, and the residue fractionated under diminished pressure.

In the cases of menthyl α-bromovalerate and menthyl α-bromohexoate, the free acids were employed, and converted to their chlorides by warming with the theoretical amount of thionyl chloride at about 60°. Any thionyl chloride which remained unattacked, together with the last traces of sulphur dioxide and hydrogen chloride, was then removed by heating the mixture on the water-bath in a vacuum. It was found unnecessary here to employ chloroform as a diluent, and the requisite amount of menthol was simply added to the reaction vessel, which was then heated at 100° for two hours under diminished pressure, and the product fractionally distilled in a vacuum.

All five esters were further purified by a repetition of the vacuum distillation process; they are pleasant smelling, colourless, and somewhat viscous oils. Their boiling points, and the results of the analyses made of the compounds, are appended in tabular form:

					Found.		Theory.	
Menthyl.	B.p.	Subst.	CO_2.	H_2O.	C.	H.	C.	H.
Bromoacetate	177—178°/40 mm.	0·1267	0·2420	0·0931	52·09	8·16	51·99	7·58 per cent.
α-Bromopropionate ...	164°/30 mm.	0·1556	0·3096	0·1036	54·25	7·40	53·60	7·90 per cent.
α-Bromobutyrate	174°/30 mm.	0·1146	0·2316	0·0887	55·11	8·60	55·08	8·20 per cent.
α-Bromovalerate	180—185°/25 mm.	0·1188	0·2475	0·0960	56·80	8·98	55·43	8·47 per cent.
α-Bromohexoate	185—190°/20 mm.	0·0952	0·1987	0·0744	56·94	8·69	57·66	8·71 per cent.

Menthyl α-bromomyristate, $CH_3\cdot[CH_2]_{11}\cdot CHBr\cdot CO_2\cdot C_{10}H_{19}$, was prepared from the chloride of α-bromomyristic acid (obtained as indicated in the cases of α-bromo-valeric and -hexoic acids) and menthol under diminished pressure at 100°. It crystallised in colourless, wax-like tablets from alcohol, and melted at 26°.

Menthyl α-bromopalmitate, $CH_3\cdot[CH_2]_{13}\cdot CHBr\cdot CO_2\cdot C_{10}H_{19}$, was produced in an analogous manner to the last-described ester, and separated from ether in soft, white crystals, which melted at 29—30°:

0·1087 gave 0·2617 CO_2 and 0·1055 H_2O. C = 65·66; H = 10·78.

$C_{26}H_{49}O_2Br$ requires C = 65·97; H = 10·36 per cent.

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XXIII.—*The Preparation of Conductivity Water.*

By FERDINAND BERNARD THOLE.

OF the numerous forms of apparatus that have been described for the preparation of conductivity water, particular mention may be made of those designed by Bousfield (Trans., 1905, **87**, 740), and by Hartley, Campbell, and Poole (Trans., 1908, **93**, 428).

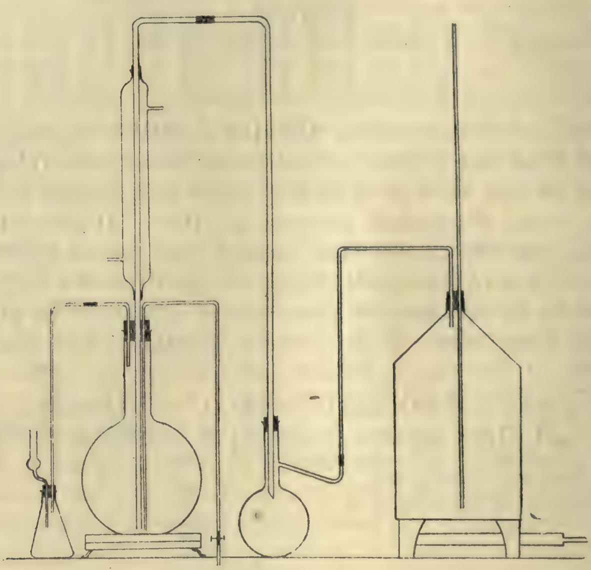
In the former apparatus the condenser consisted of a copper box containing four hard glass or platinum tubes, through which the cooling water flowed, the condensed water from each tube being collected separately.

In this apparatus the purest water was obtained from the coldest tubes, and had K_{18} 1·1 to 1·2 gemmhos under the best, and K_{18} 1·7 gemmhos under ordinary laboratory conditions.

Hartley's apparatus is somewhat simpler in construction, one condenser of block tin being used, and, moreover, it possesses the advantage that the only communication between the water and the outside air lies through a suitably connected soda-lime tube. Starting with fairly good distilled water, a fraction of very pure water (K_{18} 0·75 gemmhos) was obtained under ordinary laboratory conditions.

Having had occasion to use considerable quantities of conductivity water, the author's attention has been drawn particularly to two points in the above-mentioned types of apparatus:

FIG. 1.



(1) The condensers are somewhat complex and expensive, and cannot be made from ordinary laboratory materials.

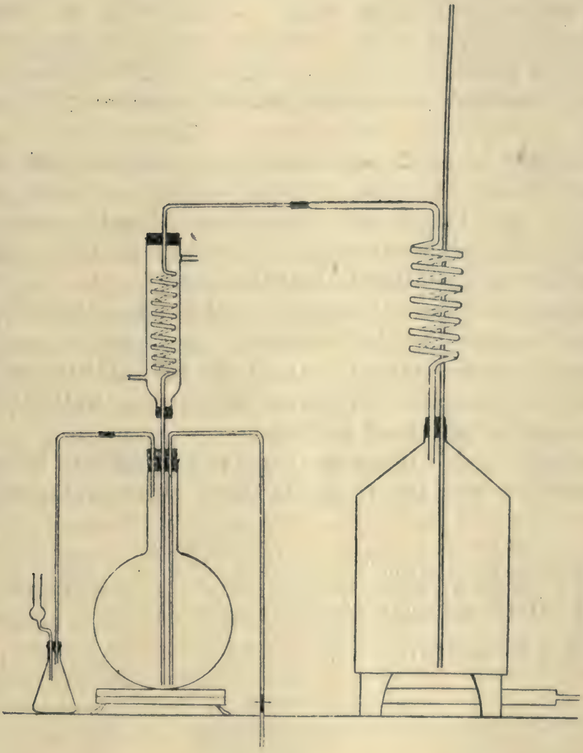
(2) The water is completely cooled before collection, and therefore the carbon dioxide and ammonia present are removed from the apparatus comparatively slowly.

If the apparatus were so constructed that pure steam could be blown through the collected water, these impurities, which constitute the major portion of the impurities in conductivity water, would be more readily and rapidly removed. Bousfield, in fact, found that when his water was boiled in a platinum bottle its conductivity fell considerably.

The two forms of apparatus figured below have been constructed with a view to overcoming these two drawbacks, and have given good results in the author's hands during the past year.

The first apparatus (Fig. 1) may be readily constructed from ordinary laboratory materials. A large steam generator is connected with a distilling bulb and column, which act as a spray trap. The steam thus purified passes through a Liebig condenser to the bottom of the receiving flask, which is fitted with a rubber stopper carrying a syphon and a soda-lime tube of the type described by Hartley, Campbell, and Poole.

FIG. 2.



The flask stands on an electrically heated plate, and all glass parts of the apparatus in contact with the steam and purified water are constructed of well steamed Jena glass.

Fig. 2 represents a more compact form of the same apparatus, the chief modification being the spiral spray trap which returns condensed liquid to the boiler.

The cost of this form is very small, and the water obtained, although not as pure as that obtained by Hartley, is, however, of sufficient purity for all ordinary purposes. The preparation is conducted as follows:

The boiler is filled with ordinary distilled water, which is allowed to boil gently for twenty minutes before connexion is made with the condenser and receiver. The next fraction (about 1½ litres) has an average conductivity of 1·8 gemmhos (25°). This value may be considerably reduced by allowing a rapid current of steam to pass through the contents of the flask. At this stage the distillate is run off and the purest fraction collected, the steam being condensed as rapidly as possible. With a six-litre boiler two litres of water having an average conductivity of 1·5 gemmhos (25°) may be collected.

If the supply of condensed water is now stopped, and the plate electrically heated, the water is rapidly raised to boiling, and the conductivity falls to 1·3 or 1·2 gemmhos. Slightly better results have been obtained by stopping the supply of steam, and using only the heat of the plate to boil the water.

Test experiments under varying conditions show that it is almost immaterial whether distilled water or tap water is used in the boiler, and no advantage is gained by the addition of sodium hydroxide or potassium hydrogen sulphate. Both forms of apparatus give equally good products.

The appended table shows the average conductivity in gemmhos of the products obtained from the forms of apparatus mentioned above:

Bousfield.	Hartley.	Thole.
K_{18} 1·7 (in London laboratory).	K_{18} 0·75.	K_{25} 1·3—1·2.
K_{18} 1·1 (in private laboratory).		K_{18} 1·1—1·0.
K_{18} 0·8 (boiled in platinum bottle).		

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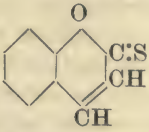
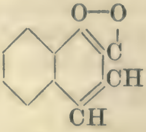
XXIV.—*The Thio-analogues of Coumarin and its Derivatives.*

By Arthur Clayton and William Godden.

It has been shown that the homologues of coumarin, like coumarin itself, can be converted into the corresponding thio-compounds by heating with phosphorus pentasulphide, and that the thiocoumarins so obtained are characterised by their ability to yield oximes and hydrazones, this property not being exhibited by the coumarins themselves (Clayton, Trans., 1908, **93**, 524). The difference thus indicated in the constitutions of the coumarins and thiocoumarins finds expression in the subjoined formulæ, where thiocoumarin is represented as a thioketone, whilst coumarin is assigned a different but similar structure:



Thiocoumarin.



Coumarin.

In order to ascertain whether the above structural difference exists in the derivatives of coumarin and thiocoumarin, and also in view of the fact that no nitrothiocoumarins have heretofore been prepared, the authors have made a study of the methods of preparation and properties of these compounds.

Preliminary attempts to prepare nitrothiocoumarins showed that the ordinary method of preparation (that is, simply fusing the coumarin with phosphorus pentasulphide) was not applicable, as the mixture caught fire before thionation took place. This inflammation is doubtless due to sudden oxidation by the nitro-group. The preparation was successfully accomplished, however, by heating phosphorus pentasulphide with a solution of the coumarin in toluene, xylene, or a mixture of these solvents.

In this manner were obtained 6-*nitrothiocoumarin*, 8-*nitrothiocoumarin*, 6-*nitro*-7-*methylthiocoumarin*, 5-*nitro*-6 : 7-*dimethylthiocoumarin*, 5-*nitro*-4 : 6 : 8-*trimethylthiocoumarin*, 5-*nitro*-4 : 6 : 7-*trimethylthiocoumarin*, 6 : 7-*dimethylthiocoumarin*, 4 : 6 : 7-*trimethylthiocoumarin*, and 4 : 6 : 8-*trimethylthiocoumarin*. The constitution of these compounds was shown in each case by partial oxidation with nitric acid or chromic acid, the parent coumarin or nitrocoumarin being obtained in every instance.

Unlike the nitrocoumarins, which are colourless, the nitrothiocoumarins are characterised by a deep yellow colour, which in some cases is intensified to a magnificent golden-red. They have the general properties of thiocoumarin, for 6-nitrothiocoumarin yields a hydrazone, an oxime, and an amorphous and insoluble mercurichloride, thus showing that the ketonic structure of thiocoumarin is preserved not only in its homologues, but also in its nitro-derivatives.

This renders it highly probable that the difference of constitution exhibited by coumarin and thiocoumarin is purely due to the different functions fulfilled by the oxygen and sulphur atoms, and unaltered by substitution in the rest of the molecule. The localisation of the cause of the difference of properties exhibited by coumarin and thiocoumarin, when treated with phenylhydrazine and hydroxylamine, may involve a principle of wide application. The functions of the oxygen and sulphur atoms in this and similar series will be dealt with in a forthcoming paper.

Throughout the whole series of the thiocoumarins there appeared a strong tendency towards reversion to the coumarins whenever the molecules entered into reaction; thus it is impossible to nitrate thiocoumarins under any conditions, and even an attempt to reduce 6-nitrothiocoumarin with stannous chloride resulted in the formation of 6-nitrocoumarin and 6-aminocoumarin. Bromine also converts thiocoumarin into coumarin. Notwithstanding the apparent looseness of combination of the sulphur atom, this element cannot be removed from thiocoumarin by prolonged boiling in xylene solution with sodium, copper powder, or aluminium powder.

It was noted in an earlier communication (Clayton, Trans., 1908, **93**, 529) that in the preparation of thiocoumarins by heating the coumarin with phosphorus pentasulphide in the dry state, the product contained loosely combined sulphur, which was only removed by repeated crystallisation, or by treatment with copper powder. The same peculiarity was noticed in preparing thiocoumarins by the new method, although the nitrothiocoumarins always appeared to be free from this adherent sulphur. Thiocoumarin was therefore heated with a molecular proportion of sulphur, both in solution in boiling carbon disulphide, and in the dry state, to 160°, with the object of preparing a persulphide, but in each case the thiocoumarin was recovered unchanged. It is therefore probable that the loosely combined sulphur is present in the form of a molecular compound of thiocoumarin and some other compound containing sulphur.

It has also been noted that the nitrocoumarins, except those with a nitro-group in the lactonic ring, are colourless (Clayton, Trans., 1910, **97**, 1350, 1388, *et seq.*), the only exception being 8-nitrocoumarin, which is described by Miller and Kinkelin as possessing a yellow colour (*Ber.*, 1889, **22**, 1706). The authors repeated the preparation of the compound in the manner indicated by these investigators, and confirmed their results, but it was found that if 8-nitrothiocoumarin is carefully purified, and then oxidised to 8-nitrocoumarin, the latter compound is obtained quite white. It may therefore be taken as proved that the nitrocoumarins are colourless unless they contain a nitro-group in the lactonic ring.

The method of thionation described in this paper is not applicable to the 3-nitro-substituted coumarins, as these compounds are either destroyed or unaltered under the treatment, the nitro-group in the α-position with regard to the "carbonyl" group apparently exerting a repellent action on the sulphur atom.

Attempts to prepare the aminothiocoumarins were not successful, complete destruction apparently taking place when 6-aminocoumarin or its acetyl derivative was heated with phosphorus pentasulphide alone, or in boiling xylene. Treatment of the nitrothiocoumarins with reducing agents likewise proved abortive.

EXPERIMENTAL.

6-*Nitrothiocoumarin.*—6-Nitrocoumarin (1 part) and finely powdered phosphorus pentasulphide (2·5 parts) were mixed together and well covered with xylene. The mixture was then boiled for two hours, and the liquid filtered. On cooling, crystals separated in abundance. These were dissolved in boiling glacial acetic acid, and filtered from some insoluble matter separated by this solvent, when from the cold liquid a plentiful crop of splendid golden-brown needles, melting at 229°, were obtained, the yield being 80 per cent. of that indicated by theory. These crystals, when shaken with alcohol and yellow mercuric oxide for one and a-half hours, or when treated with nitric acid, regenerated 6-nitrocoumarin:

0·3300 gave 0·3680 $BaSO_4$. S = 15·28.
0·2736 ,, 15·9 c.c. N_2 at 17° and 759 mm. N = 6·74.
$C_9H_5O_3NS$ requires S = 15·46; N = 6·76 per cent.

6-*Nitrocoumarinoxime.*—6-Nitrothiocoumarin (10 parts), sodium hydroxide (3 parts), and hydroxylamine hydrochloride (5 parts) were boiled in alcoholic solution for six days, after which the liquid was filtered and allowed to cool. Pale yellow, feathery needles were obtained, melting at 249—250°:

0·1060 gave 12·1 c.c. N_2 at 15° and 760 mm. N = 13·37.
$C_9H_6O_4N_2$ requires N = 13·59 per cent.

6-*Nitrocoumarinphenylhydrazone.*—6-Nitrothiocoumarin (10 parts) and phenylhydrazine (5·2 parts) were dissolved in alcohol, and boiled until no more hydrogen sulphide was evolved (four days), after which the solution was filtered, and then yielded red needles, which, when crystallised from glacial acetic acid, melted at 213°:

0·1120 gave 14·2 c.c. N_2 at 15° and 767·5 mm. N = 14·99.
$C_{15}H_{11}O_3N_3$ requires N = 14·94 per cent.

6-*Nitrocoumarin Mercurichloride.*—6-Nitrothiocoumarin (5 parts) and mercuric chloride (6·5 parts) were separately dissolved in the smallest possible quantity of ether, and the solutions then mixed together. After about an hour the mercurichloride separated as a yellowish-white powder. The product can as easily be obtained from alcoholic solutions:

0·2520 gave 0·1259 $BaSO_4$. S=6·85.

$C_9H_5O_3NS,HgCl_2$ requires S=6·69 per cent.

8-*Nitrothiocoumarin.*—This substance was prepared in exactly the same way as 6-nitrothiocoumarin, and when crystallised from glacial acetic acid formed fine, golden-brown crystals, melting at 195—196°:

0·1962 gave 0·2194 $BaSO_4$. S=15·46.

$C_9H_5O_4NS$ requires S=15·46 per cent.

When warmed with nitric acid (D 1·5), 8-nitrocoumarin was regenerated, which, after crystallisation from glacial acetic acid, formed white needles (compare Miller and Kinkelin, *Ber.*, 1889, **22**, 1706).

6-*Nitro-7-methylthiocoumarin.*—This compound was easily obtained by the general process, and after crystallisation from glacial acetic acid, formed golden-yellow, woolly crystals, melting at 202°. When treated with nitric acid (D 1·5), 6-nitro-7-methylcoumarin was obtained:

0·1170 gave 0·1211 $BaSO_4$. S=14·22.

$C_{10}H_7O_3NS$ requires S=14·48 per cent.

6:7-*Dimethylthiocoumarin.*—6:7-Dimethylcoumarin (1 part) and finely powdered phosphorus pentasulphide (1·5 parts) were boiled together in xylene for three hours. The filtered liquid yielded crystals, which, when crystallised from glacial acetic acid, formed flattened, golden-yellow needles, melting at 162—163°, and rather sparingly soluble in the usual solvents:

0·1390 gave 0·1744 $BaSO_4$. S=17·23.

$C_{11}H_{10}OS$ requires S=16·84 per cent.

5-*Nitro*-6:7-*dimethylthiocoumarin.*—The preparation was carried out in the usual manner, and gave rise to a very clean product, which crystallised from glacial acetic acid in golden-yellow needles, melting at 199—200°:

0·1440 gave 0·1376 $BaSO_4$. S=13·12.

$C_{11}H_9O_3NS$ requires S=13·62 per cent.

On adding a little chromic acid to the solution in acetic acid, 5-nitro-6: 7-dimethylcoumarin was regenerated.

4: 6: 8-*Trimethylthiocoumarin.*—4: 6: 8-Trimethylcoumarin (1 part) and finely powdered phosphorus pentasulphide (2·5 parts) were boiled together in a mixture of toluene and xylene, the xylene being added until the boiling point of the liquid became high enough to start the reaction. After two hours the liquid was filtered and evaporated to dryness, as the product is somewhat soluble in cold xylene. The residue, after crystallisation from glacial acetic acid, formed golden-yellow flakes, melting at 182—183°:

0·1345 gave 0·1604 $BaSO_4$. S=16·38.
$C_{12}H_{12}OS$ requires S=15·68 per cent.

5-*Nitro*-4 : 6 : 8-*trimethylthiocoumarin.*—This compound, readily obtained from 5-nitro-4 : 6 : 8-trimethylcoumarin by the usual treatment with phosphorus pentasulphide in xylene, is fairly soluble in the latter solvent. The solution was therefore evaporated to dryness, and the residue crystallised from glacial acetic acid. The substance then formed golden needles, melting at 181—182°:

0·1452 gave 0·1350 $BaSO_4$. S=12·77.
$C_{12}H_{11}O_3NS$ requires S=12·85 per cent.

4 : 6 : 7-*Trimethylthiocoumarin.*—The preparation of this substance from 4 : 6 : 7-trimethylcoumarin was accomplished by the usual process, but the product possessed a dark colour, which was only removed by repeated crystallisation from glacial acetic acid. During the heating with phosphorus pentasulphide, a purple coloration made its appearance, and it was found advisable to keep the temperature from rising unnecessarily, as the coloration was more developed at higher temperatures, and the product became correspondingly impure:

0·1238 gave 0·1450 $BaSO_4$. S=16·01.
$C_{12}H_{12}OS$ requires S=15·68 per cent.

5-*Nitro*-4 : 6 : 7-*trimethylthiocoumarin.*—This substance was obtained in the usual manner by the thionation of 5-nitro-4 : 6 : 7-trimethylcoumarin in xylene solution. It crystallises from glacial acetic acid in golden-brown needles, melting at 180—181°:

0·3194 gave 0·2870 $BaSO_4$. S=12·34.
$C_{12}H_{11}O_3NS$ requires S=12·85 per cent.

When treated with nitric acid (D 1·4), 5-nitro-4 : 6 : 7-trimethylcoumarin is regenerated.

In general, the method of thionation described in this paper is specially applicable to the nitrocoumarins, an unfavourable result being obtained only in the case of 3 : 6-dinitro-4 : 7-dimethylcoumarin, which yielded a small quantity of a mixture of brown needles and colourless, transparent, micaceous plates. Decomposition during thionation was always attended by the appearance of a purple coloration, but in the preparation of the nitrothiocoumarins this colour rarely appeared, the liquid remaining of a red colour and free from tarry matter. In such cases the yield approached the theoretical.

The authors desire to express their thanks to the Research Fund Committee of the Chemical Society for a grant which has in part defrayed the expense incurred during this research.

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XXV.—*Nitrites of the Alkylammonium Series. Part III.* Triethylammonium Nitrite and its Decomposition and Sublimation by Heat.*†

By Prafulla Chandra Rây and Jitendra Nath Rakshit.

This communication has been somewhat delayed on account of the difficulty experienced in obtaining triethylamine in a state of purity. Our first attempt was to obtain tetraethylammonium bromide according to the method described by Scott (Trans., 1909, **95**, 1200), and from it the corresponding hydroxide which, under the action of heat, decomposes into triethylamine, ethylene, and water. Although we closely followed Scott's directions, we invariably obtained, in three separate experiments, monoethylamine. It has been found that by the interaction of ammonia and its equivalent of ethyl bromide, the primary amine is always formed, and this reaction is practically finished in twenty-four hours, the bottle containing the mixture remaining sensibly warm during this length of time. Subsequent addition of sodium hydroxide does not lead to the formation of the higher alkylated ammonias, but gives rise only to the production of ether and sodium bromide. Presumably the higher temperature of the Calcutta laboratory (32—35°) plays an important part in this reaction. We now naturally turned towards Hofmann's classical researches on the subject (*Phil. Trans.*, 1850, Pt. I., 121). Although the details have not been given of the exact circumstances in which mono-, di-, and tri-ethylamine respectively are formed, after several repetitions of the experiments we hit on the conditions under which each of these can be conveniently prepared. The preparation of the tertiary amine is rather difficult, "which," to quote the language of the discoverer himself, "is the result of a long series of troublesome and expensive processes" (*loc. cit.*, p. 359). The triethylamine we obtained, when distilled over solid potassium hydroxide, boiled constantly at 91°. It was converted into the platinichloride (Found, Pt=31·76. Calc., Pt=31·86 per cent.), which has the remarkable property of fusing at 100°, as noticed by Hofmann.

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* The abstract of this paper (Proc., 1911, **27**, 264) is wrongly numbered Part IV.

† The description of triethylammonium nitrite which has recently appeared (Trans., 1911, **99**, 1252) is evidently that of an impure substance. As practically no analysis of the salt has been given except the estimation of "nitritic" nitrogen, and as it has been found to decompose with "explosive violence," it would appear that the so-called triethylammonium nitrite was largely contaminated with ammonium nitrite; the properties of the latter, in fact, agree fairly well with the description given.

Preparation.—The two distinct methods already described (Trans., 1911, **99**, 1470) are equally applicable in this case. Mercuric nitrite or rather sodium mercuric nitrite solution was treated with aqueous triethylamine. The precipitate obtained was, however, not an alkyl substituted mercuriammonium nitrite or simply dimercuriammonium nitrite, but the orange-coloured mercuric oxide. (Found, Hg=91·77. Calc., Hg=92·5 per cent.) The filtrate containing triethylammonium nitrite and sodium nitrite was evaporated in a vacuum over sulphuric acid. The crystalline residue may now be extracted with a suitable solvent, for example, alcohol or ether, which dissolves the amine nitrite. The latter, however, is conveniently prepared by double decomposition between triethylamine hydrochloride and silver nitrite in aqueous solution and evaporation of the filtrate in a vacuum over sulphuric acid.

Properties.—The salt crystallises in glistening, pale yellow tablets and prisms, and is extremely deliquescent. Ten seconds' exposure to the damp atmosphere of Calcutta (in September) is sufficient to liquefy the crystals. It is very soluble in absolute alcohol, benzene, or chloroform, but rather sparingly so in ether. Mr. N. R. Dhar, B.Sc., has kindly undertaken the measurement of the electrical conductivity and the ionisation of the salt, and the results he has obtained are tabulated below:

Dilution in litres.	Percentage ionised.
7·7	78
23·1	86
69·3	96
623·7	100

The ionisation of this salt is thus almost quantitatively similar to that of barium nitrite. The mean temperature of experiment was 29·1°.

Analysis of the salt gave the following results[*]:

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[*] The combustion of this salt was carried out with the precautions mentioned under the analysis of methylammonium nitrite (*loc. cit.*, p. 1017), and was carried out with much less difficulty than in the latter case. It did not in the least show any tendency to "decompose with explosive violence" as mentioned by Neogi.

0·2567 gave 0·4500 CO_2 and 0·2550 H_2O. C=47·81; H=11·03.
0·1300 „ 12·16 c.c. N_2 (moist: nitritic) at 32° and 760 mm. N=10·06.

$N(C_2H_5)_3,HNO_2$ requires C=48·64; H=10·82; N("nitritic")=9·47 per cent.

Owing to the highly deliquescent nature of the substance, it was found almost impracticable to weigh out the salt in the boat without it absorbing some moisture. If the excess of water as calculated from the hydrogen (theoretical) is deducted from the weight of the salt, the percentage of carbon becomes 48·66.

Decomposition by Heat.

This salt has been found to be fairly stable at the ordinary temperature (31°) in a vacuum. On slowly raising the temperature to 45°, it begins to sublime with slight decomposition. Three samples of two distinct preparations have been found to give the above temperature as the sharp subliming point. If the temperature is maintained between 45° and 50°, a long, crystalline layer of the sublimate is deposited in the cooler parts; at the same time some portion undergoes decomposition. On raising the temperature to 60—65°, the residual salt in the bulb in direct contact with its sides begins apparently to melt at 75°, the whole mass passes into the liquid shape and bubbles are continuously given off, and the decomposition becomes fairly rapid. As among the products of decomposition there are formed various liquids, it can hardly be decided whether the molten mass is a solution of the substance in the liquid products of decomposition or the substance itself in the fused state. It has also been observed that the sublimate is washed down by the liquid products condensing in the cooler parts.

The major part of the salt decomposed at 75—80°, and finally the temperature was raised to 100°, at which it was maintained until the "click" became persistent. There was practically no residue in the bulb. The sublimate was tested and found to be a nitrite.

The liquid which passed over into the collecting tube was extracted with water and acidified with dilute sulphuric acid, and subjected to distillation. The distillate gave a copious precipitate of iodoform with sodium hydroxide and iodine. It may be mentioned here that the filtrate from the interaction of triethylamine and mercuric nitrite solution when similarly treated also responds to the iodoform test. The residual triethylamine was recovered by redistillation with excess of alkali, and was caught in hydrochloric acid and converted into the platinichloride. (Found, Pt=31·73. Calc., Pt=31·86 per cent.)

The gaseous products consisted of nitric oxide, nitrous oxide, and nitrogen. The results of analysis (for the method of analysis see Trans., 1907, **91**, 1399) are given below:

	Weight of salt. Gram.	Total gas. c.c.	NO. c.c.	N_2O. c.c.	N. c.c.
Prep. I.	0·1470	13·2	8·8	2·15	2·25
,, ...	0·1702	19·1	12·7	3·2	3·2
Prep. II.	—	18·5	12·05	3·1	3·2

It is peculiar, however, that the ratio of the three gases is in all the three experiments as 4 : 1 : 1; of course, this constancy in the ratio can only be regarded as incidental *; and in the same way the proportion of salt that sublimes unchanged depends much on the manner of bringing about the decomposition. As a rule, about half of the salt may be obtained in the sublimate.

It is of interest to note that by the interaction of triethylamine and nitrous acid (as triethylammonium nitrite potentially represents it) alcohol is formed.

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XXVI.—*The Action of Ammonia on* 6-*Chloro*-2-*phenyl*-1 : 3-*benzoxazine*-4-*one.*

By ERNEST CHISLETT HUGHES and ARTHUR WALSH TITHERLEY.

IT has already been noted by the authors (Trans., 1910, **97**, 1377) that ammonia reacts with 6-chloro-2-phenyl-1 : 3-benzoxazine-4-one (I), producing a yellow, crystalline compound. This action, which has since been studied closely, is similar to that of ammonia on 2-phenyl-1 : 3-benzoxazine-4-one (Titherley and Hughes, Trans., 1911, **99**, 1493), the yellow compound, 5-chlorosalicylbenzamidine (III), being formed from the hypothetical additive compound (II). By long-continued action of ammonia, however, in hot alcoholic solution, a pale yellow, very insoluble substance is formed, which on investigation proved to be the chloro-derivative of *o*-hydroxytriphenyltriazine (IV). This compound is also produced by the

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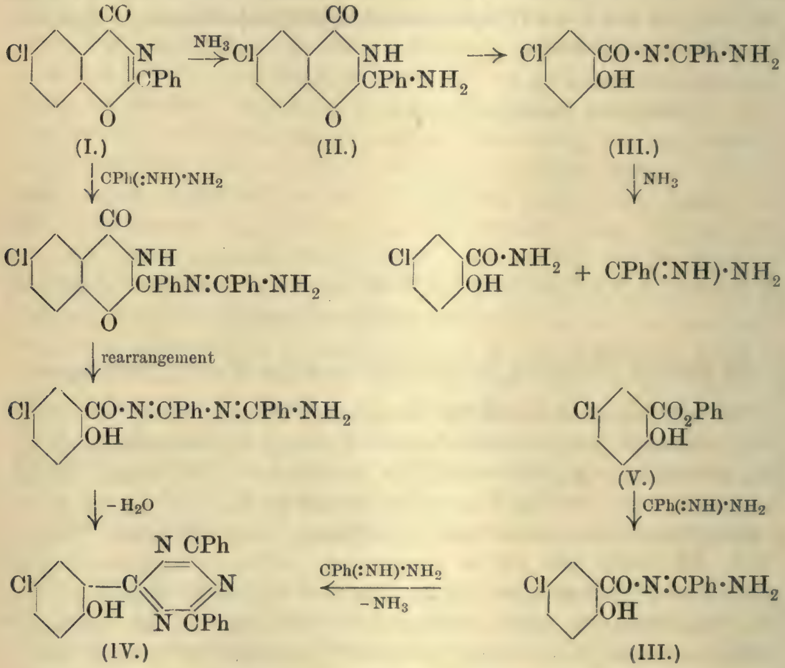
* This particular relationship between the gas volumes, which is strikingly constant, may be explained by the following equation, assuming that the highly deliquescent salt during its introduction into the decomposing tube absorbs two molecules of water for every seventeen molecules of the salt:

$$17NEt_3,HNO_2+2H_2O=12NO+3N_2O+3N_2+10Et_3+21EtOH.$$

condensation between phenyl 5-chlorosalicylate (V) and benzamidine, evidently through 5-chlorosalicylbenzamidine (III), which, from analogy to the condensation previously described (Trans., 1911, **99**, 1499) between phenyl salicylate and benzamidine, must be first formed. This assumption is confirmed by the fact that it is also obtained readily by the direct condensation of benzamidine and 5-chlorosalicylbenzamidine.

The same triazine derivative may, however, be obtained still more readily by the condensation of benzamidine and 6-chloro-2-phenyl-1:3-benzoxazine-4-one. It is therefore evident that, in the long-continued action of ammonia on the latter, a portion of the resulting 5-chlorosalicylbenzamidine must undergo ammoniolysis, yielding benzamidine, which then condenses with the remainder, producing, by addition, rearrangement, and loss of water, the triazine derivative (IV). These relations are expressed in the scheme:



The properties of 5-chlorosalicylbenzamidine and the triazine derivative are similar in all respects to the corresponding parent compounds free from chlorine, previously described (*loc. cit.*).

EXPERIMENTAL.

5-*Chlorosalicylbenzamidine*, $OH\cdot C_6H_3Cl\cdot CO\cdot N\colon CPh\cdot NH_2$.

Two grams of 6-chloro-2-phenyl-1 : 3-benzoxazine-4-one were heated with 10 c.c. of concentrated ammonia and sufficient alcohol to dissolve the solid. The resulting bright yellow solution was rapidly concentrated on the water-bath to half its bulk, when on cooling bright orange-yellow needles (2 grams) separated, consisting of 5-*chlorosalicylbenzamidine*, which after recrystallisation from light petroleum melted at 156°:

0·1304, by Kjeldahl's method, required 9·5 c.c. *N*/10-HCl. N = 10·20.

$C_{14}H_{11}O_2N_2Cl$ requires N = 10·22 per cent.

The compound is sparingly soluble in ether or light petroleum, moderately so in cold alcohol or chloroform, and readily so in acetone or hot alcohol. The acetone solution gives a strong reddish-violet coloration with ferric chloride.

5′-*Chloro*-2′-*hydroxy*-2 : 4 : 6-*triphenyl*-1 : 3 : 5-*triazine*, $OH\cdot C_6H_3Cl\cdot C_3N_3Ph_2$.

(1) This compound is formed by the continued action of ammonia on 6-chloro-2-phenyl-1 : 3-benzoxazine-4-one. Five grams were dissolved in the least possible quantity of hot alcohol, and 10 c.c. of strong ammonia added. The resulting bright yellow solution was heated on the water-bath for several hours, during which 5′-chloro-2′-hydroxy-2 : 4 : 6-triphenyl-1 : 3 : 5-triazine separated continually as a pale yellow solid. On cooling, a further quantity separated, and the whole after recrystallisation from alcohol was obtained in fine, flocculent needles, melting at 224·5°. The yield was 3 grams:

0·3748, by Kjeldahl's method, required 30·9 c.c. *N*/10-HCl. N = 11·54.

0·3902 gave 0·1532 AgCl. Cl = 9·71.

$C_{21}H_{14}ON_3Cl$ requires N = 11·61; Cl = 9·82 per cent.

The compound is very sparingly soluble in the usual solvents in the cold except acetone, in which it is moderately soluble. It is somewhat soluble in hot light petroleum, benzene, or alcohol, from which it crystallises in characteristic matted needles on cooling. It dissolves in concentrated sulphuric acid with a bright red colour, which disappears on warming. The compound does not show phenolic properties, and it is not affected by sodium in boiling benzene solution or phosphorus pentachloride in boiling chloroform solution.

(2) *Preparation from* 6-*Chloro*-2-*phenyl*-1 : 3-*benzoxazine*-4-*one*.—One gram of the chloro-derivative dissolved in hot alcohol was

treated in alcoholic solution with 0·35 gram of benzamidine freshly prepared from 0·5 gram of its hydrochloride. A bright orange solution immediately resulted, which in a few seconds gave place to a thick mass of pale yellow needles, which after washing with boiling alcohol melted at 223°. The yield was 1 gram, and a further 0·3 gram was recovered from the mother liquor. The substance was identical with 5′-chloro-2′-hydroxy-2:4:6-triphenyl-1:3:5-triazine obtained by method (I), and a mixture of the two melted at 223°.

(3) *Preparation from 5-Chlorosalicylbenzamidine.*—One gram of 5-chlorosalicylbenzamidine in alcoholic solution was heated to boiling with 0·35 gram of benzamidine for several hours. Slow action took place, and 5′-chloro-2′-hydroxy-2:4:6-triphenyl-1:3:5-triazine was continually deposited in a pure form as pale yellow needles melting at 222° (yield, 0·3 gram).

(4) *Preparation from Phenyl 5-Chlorosalicylate.*—One gram of phenyl 5-chlorosalicylate in alcoholic solution was heated to boiling with 0·5 gram of freshly prepared benzamidine. A yellow solution was obtained, and after several hours a voluminous, pale yellow precipitate of pure 5′-chloro-2′-hydroxy-2:4:6-triphenyl-1:3:5-triazine was obtained (m. p. 220°), phenol being eliminated. The yield was 0·3 gram.

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XXVII.—*An Experimental Investigation of the Bleaching Process.*

By SYDNEY HERBERT HIGGINS.

IN reply to Taylor's criticism (Trans., 1911, **99**, 1906) of the author's previous paper (*ibid.*, p. 858), experiments are now described which point to the conclusion that hypochlorites bleach because they produce nascent oxygen directly, and that bleaching cannot be due to free chlorine, since chlorine-water is a comparatively weak bleaching agent. The subject under discussion thus becomes divided into two distinct parts: (1) the production of chlorine from hypochlorites, and (2) the stimulation of the bleaching properties of hypochlorite solutions.

As regards (1) the present author put forward a reversible action, which was founded on actual observations and explained all Taylor's results; the assumptions that the action of chlorine on alkalis was a reversible action, and that carbon dioxide liberated hydrochloric acid from its salts did not require to be made. Taylor, however, divided the equation given by the author into two parts, and in so doing supported the contention that chlorine-water contains hypochlorous acid. Now, since chlorine bleaches only in the presence of water, and since Taylor now states that chlorine and water yield hypochlorous acid, it is to be inferred that the bleaching is due to hypochlorous acid. This matter is referred to later. As regards (2)—the stimulation of the bleaching properties of hypochlorites—the present author only considered the action of the carbon dioxide of the air in cases of bleaching under ordinary conditions; he did not, as Taylor states, discuss any experiments in closed vessels from that point of view. To explain the action of neutral salts on hypochlorite solutions contained in closed vessels, the catalytic action of neutral salts was mentioned. The author has been unable to find any previous work on the catalytic action of neutral salts on hypochlorites; but seeing that a similarity is drawn later between the properties of hydrogen peroxide and of hypochlorous acid, it is interesting to record the statement of Thenard (*Ann. Chim. Phys.*, 1818, **9**, 314), that all substances exert some catalytic action on hydrogen peroxide, either increasing or decreasing its stability. As regards the catalytic action of neutral salts, Buchböck (*Zeitsch. physikal. Chem.*, 1897, **23**, 123; 1900, **34**, 229) showed that solutions of a large number of neutral salts affected the velocity of the decomposition of carbonyl sulphide; Tammann (*Zeitsch. physikal. Chem.*, 1892, **9**, 106) found that 0·4 gram-molecule of sodium chloride increased the rate of inversion of sucrose 26 per cent.; and it was also shown that potassium and sodium sulphates accelerated the rate of hydrolysis of an ester, although not to the same extent as they influenced the rate of inversion of sucrose. The author contends that his experiments point to neutral salts having a catalytic influence on the stability of hypochlorite solutions; this influence might be a great or small acceleration, or even a retardation of the rate of decomposition, according to the concentration, etc., just as has been noticed in other cases of catalytic action. Further experiments now given by Taylor are not described in sufficient detail to admit of repetition or full criticism. The only experiments of which any details are given were performed with 10 c.c. of bleaching liquor, in which small pieces of wetted out Turkey-red cloth were immersed. It is true that the cloth was squeezed before immersion, but even then this method would lead to the introduction of varying amounts of water along with the cloth to augment the volumes of the extremely small bleaching baths, and thus produce untrustworthy results. Moreover, the addition of the neutral salts in the solid state to the bleaching liquors would produce varying degrees of cooling, and cause an irregular retardation of the bleaching action. Taylor made his tests on the bleaching of Turkey-red cloth, and judged his results from the appearance of that cloth; but the present author found titrations more convincing than ocular observations, and the oxidation of the natural colouring matters of textile fibres of more importance than the oxidation of alizarin red lakes. Nevertheless, Taylor admits that salts other than chlorides act in some degree as chlorides do in bleaching cisterns; but his equations do not explain this fact. Nor is any explanation given of the fact that common salt stimulates the bleaching action of bleaching powder solution which has been exposed to air just as does calcium chloride (Trans., 1911, **99**, 865). The author describes below further experiments supporting previously formed conclusions.

EXPERIMENTAL.

40·3 Grams of linen, which having been previously boiled to remove the waxy matters did not require wetting out, were placed in 500 c.c. of potassium hypochlorite solution prepared from bleaching powder, and the same weight of linen was put into the same volume of the hypochlorite, but containing some sodium sulphate in solution; 25 c.c. of solution were titrated to give the following results:

	KOCl.	$KOCl + Na_2SO_4$
Original	13·7	13·7 c.c. *N*/10-thiosulphate.
After 30 minutes	8·7	7·8
,, 1 hour	7·4	6·3
,, 2½ hours	4·8	3·7

It is thus seen that the presence of the sodium sulphate stimulates the bleaching action of the potassium hypochlorite solution, although this salt could play no part in the equations by means of which Taylor would explain this reaction. In a further experiment the conditions were identical with those described, except that bleaching powder solution was used in place of the potassium hypochlorite and calcium nitrate added in place of the sodium sulphate. The following results were obtained:

	Bleaching powder solution.	$+ Ca(NO_3)_2$
Original	21·3	21·3 c.c. *N*/10-thiosulphate.
After ½ hour	18·3	18·1
,, 1½ hours	16·6	16·25

It is seen that calcium nitrate, like calcium chloride, stimulates the bleaching efficiency of bleaching powder solution.

Rate of Evolution of Oxygen from Bleaching Powder Solution and from Sodium Peroxide Solution by Copper Oxide.

For this and other experiments, a number of 100 c.c. Jena-glass flasks, each fitted with india-rubber stoppers through which glass tubes passed, were used. These tubes were bent twice at right angles outside the flasks, and terminated under burettes filled with water, and standing in basins of that liquid. By this means the volume of gas evolved from the contents of each flask was found.

One hundred c.c. of bleaching powder solution (D 1·04) and 1 gram of powdered copper oxide were placed in one of the flasks, and the amount of oxygen evolved was measured at intervals:

After	3	hours	28 c.c. of oxygen
,,	6	,,	58 ,, ,,
,,	19½	,,	197 ,, ,,
,,	24	,,	234 ,, ,,
,,	27	,,	256 ,, ,,
After	30	hours	276 c.c. of oxygen
,,	44	,,	350 ,, ,,
,,	51	,,	379 ,, ,,
,,	72	,,	414 ,, ,,
,,	96	,,	430 ,, ,,

At the same time 100 c.c. of the original bleaching powder solution were titrated with $N/10$-sodium thiosulphate solution after adding potassium iodide and acidifying, when it was found that 430 c.c. of oxygen represented practically the whole of the oxygen contained in the original solution. Titration after the evolution showed that there was still a little oxygen left in solution.

A solution of sodium peroxide containing approximately the same amount of active oxygen (shown by liberation of iodine and titration) per litre as the bleaching powder solution of D 1·04 was now made, and 100 c.c. were introduced into the flask of the apparatus, along with a very small quantity of copper oxide. The amount of gas evolved was read as before:

After	½	hour	35 c.c. of oxygen
,,	1	,,	100 ,, ,,
,,	1½	hours	170 ,, ,,
,,	2	,,	230 ,, ,,
,,	2½	,,	293 ,, ,,
After	3½	hours	385 c.c. of oxygen
,,	4	,,	404 ,, ,,
,,	5	,,	410 , ,,
,,	6	,,	416 ,, ,

The results given in the two above tables were plotted in curves, suitable units being taken. The curves were found to be very similar in nature, the evolution of the oxygen being a somewhat steady one at the beginning of the action, but towards the end the last traces of the gas were only evolved very slowly. For the complete evolution of the oxygen a long time was required. The copper oxide merely accelerates the evolution of the oxygen gas, for hypochlorites themselves are found to give off pure oxygen. The author therefore maintains that during bleaching the oxidisable matter present uses up the oxygen, which is otherwise evolved as gas. This contention is supported by the fact that any agency which assists the production of oxygen from a hypochlorite solution while in contact with copper oxide, such as heat, exposure to air, addition of acid, is also found to assist the bleaching action of that hypochlorite solution.

Analogy between the Bleaching Actions of Solutions of Bleaching Powder and of Sodium Peroxide.

During bleaching with sodium peroxide solution, samples were periodically taken, and made to give off their oxygen by adding a little copper oxide in the flask of the apparatus previously described. In this way the amount of oxygen left in the bleaching bath at any time was found, and the rate of decomposition ascertained:

	Oxygen remaining in solution, in c.c.	Oxygen used up.
Original, 100 c.c.	14·3	—
After 1 hour........................	8·5	5·8
,, 2 hours	6·3	8·0
,, 3 ,, ...	5·0	9·3
,, 4 ,, ...	4·9	9·4
,, 5 ,, ...	4·8	9·5

Tests were also made from bleaching cisterns containing bleaching powder solution instead of sodium peroxide. Samples were titrated at intervals with sodium thiosulphate solution after adding potassium iodide and acidifying:

	Thiosulphate, in c.c.	Measure of oxygen used up.
Original	27·0	—
After 1 hour	16·7	10·3
,, 2 hours, 40 mins.........	11·7	15·3
,, 3 ,, 40 ,, ...	10·2	16·8
,, 4 ,, 40 ,, ...	8·9	18·1
,, 6 ,, ...	8·0	19·0

It is here worthy of mention that the author has found the method described for estimating sodium peroxide is the best one—it is almost identical with that of Archbutt (*Analyst*, 1895, 3). When sodium peroxide is used as a bleaching agent, it is generally mixed with other substances to increase the density of the solution, and, moreover, during the bleaching process, other foreign substances are introduced into the solution. These foreign substances interfere with the ordinary titrations with potassium permanganate or sodium thiosulphate. Indeed, the author found conflicting results when applying the two methods to the solutions mentioned, and had to abandon them. The oxygen evolution method, however, gave good results. It can also be used to advantage in testing spent hydrogen peroxide baths. The results shown in the two tables given above were again plotted, and using suitable units were placed alongside the other two curves for the evolution of oxygen. It was seen that all four curves were remarkably similar, pointing to the identical nature of the actions taking place in the four cases, and proving that during the bleaching action hypochlorites produce nascent oxygen directly, thus:

$$(1)\ Ca(OCl)_2 = CaCl_2 + 2O.$$
$$(2)\ NaOCl = NaCl + O.$$
$$(3)\ HOCl = HCl + O.$$

just as $H_2O_2 = H_2O + O$.

It is true that this proposition could not be fully maintained without a careful study of the chemical change taking place during the reactions described and by suitable mathematical treatment. As the bleaching tests were taken during large scale operations, where there are so many outside influences, and as during the actions with copper oxide no attempt was made to keep a constant temperature and a constant surface of oxide exposed, no mathematical deductions are expected from these figures, but an analogy is shown, and the author intends to return to the mathematical treatment.

Equation (3) is included because from a study of the action of hypochlorites and of hypochlorous acid on metals (White, *J. Soc. Chem. Ind.*, 1903, **22**, 132) and of the observations of Taylor (*loc. cit.*), one is led to the conclusion that hypochlorous acid exists in hypochlorite solutions due to the hydrolysis of the salts. Hypochlorous acid being less stable than hypochlorite solutions, it has a greater bleaching efficiency, hence the efficiency of any hypochlorite solution will largely depend on its state of hydrolysis.

The Bleaching Action of Chlorine Water.

Jakowkin (*Zeitsch. physikal. Chem.*, 1899, **29**, 613) states that chlorine-water contains hydrochloric and hypochlorous acid, produced by the reversible action:

$$Cl_2Aq + H_2O = (HCl + HOCl)Aq.$$

Richardson (Trans., 1903, **83**, 380) found on distilling chlorine-water that hypochlorous acid passed over, so that there is evidence that chlorine-water contains hypochlorous acid. In explaining the action of chlorine on water, Davy's original explanation:

$$Cl_2 + H_2O = 2HCl + O,$$

is usually accepted, and this direct production of oxygen is used to explain the bleaching action of chlorine gas; but the facts stated above point to the conclusion that chlorine acts on water in two steps, thus:

$$H_2O + Cl_2 = HCl + HOCl,$$
$$HOCl = HCl + O.$$

Moreover, it is probable that chlorine owes its bleaching properties to the existence of hypochlorous acid in its solutions. The following experiments bearing on this point were performed.

Comparison of the Rates of Bleaching of Chlorine-Water and of Bleaching Powder Solution.

A freshly prepared solution of chlorine-water was titrated with $N/10$-sodium thiosulphate solution after adding potassium iodide and acidifying, when it was found that 10 c.c. of the chlorine-water required 10·1 c.c. of the thiosulphate. A solution of bleaching powder of the same strength was made, and into 500 c.c. of the chlorine-water and of the bleaching powder solution 19 grams of boiled linen were placed. It was noticed that the linen in the bleaching powder solution soon began to lose its brown colour and became white, whereas the chlorine-water had very little bleaching effect; after one and a-half hours, the linen in the bleaching powder solution had become almost white, and the other sample remained brown in spite of the fact that a large amount of chlorine still remained in solution. Another sample of chlorine-water was produced by adding an excess of hydrochloric acid to a solution of bleaching powder, and the bleaching efficiency of this solution was compared with that of untreated bleaching powder solution of the same strength. Again it was found that the hypochlorite solution had far greater bleaching properties than the chlorine-water; in the one case, the linen became white in two and three-quarter hours, whilst in the other, after twenty-one hours' immersion it was still brown. Boiled cotton cloth, on saturating with bleaching powder solution and with chlorine-water, was found to show a similar distinction. From the above results it is evident that the addition of hydrochloric acid to bleaching powder solution does not always increase the bleaching efficiency of that solution. The experiments also show that the bleaching action of hypochlorites cannot be due to free chlorine, as Taylor has stated. On the other hand, it is probable that the small bleaching power of chlorine-water is due to the presence of some hypochlorous acid in solution.

The Bleaching Properties of the Hypochlorites of the Alkali Metals.

It has been frequently stated that the hypochlorites of lithium, sodium, and potassium have different bleaching efficiencies, the base to which the hypochlorous acid is united playing an important part in the bleaching action. Lithium hypochlorite is said to bleach better than sodium hypochlorite, which itself is said to have a greater efficiency than potassium hypochlorite. The following experiments were performed to ascertain the truth of these statements.

Solutions of the sulphates of lithium, sodium, and potassium were made containing equivalent proportions of the salts. A volume of bleaching powder solution (D 1·08) was then carefully precipitated by some of the solution of sodium sulphate until the latter salt was in slight excess. Two equal volumes of bleaching powder solution were then precipitated by adding volumes of the solutions of lithium and potassium sulphate equal to that of the sodium sulphate solution required for the precipitation in the first case. In all three cases the precipitate of calcium sulphate was allowed to settle, and then filtered off to give solutions of the hypochlorites of lithium, sodium, and potassium. These solutions contained a slight excess of the alkali sulphate in each case, but these being in equivalent proportions would have approximately the same effect on the bleaching properties of each solution (Higgins, Trans., 1911, **99**, 858). Moreover, small quantities of the hydroxides of the different metals were present in each solution, produced by the interaction of the alkali sulphates and the small quantity of free lime contained in the bleaching powder solution used.

Bleaching Properties of the Solutions.

To 500 c.c. of each of the solutions was added 500 c.c. of water, and after titrating 10 c.c. of the mixture with *N*/10-sodium thiosulphate (after adding potassium iodide and acidifying), 23·6 grams of boiled linen were introduced into each solution. After one hour's bleaching titrations were again made:

	Li.	Na.	K.
Original	9·1	9·1	9·1 c.c. of *N*/10-thiosulphate
After 1 hour	8·1	8·1	8·1

The original solution used in a second test was made weaker than that used in the above experiment. The following results were obtained:

	Li.	Na.	K.
Original	3·7	3·8	3·8 c.c. of *N*/10-thiosulphate
After 30 mins.' bleaching	2·5	2·7	2·6
,, 1 hour's ,,	2·2	2·5	2·5
,, 2 ,, ,,	1·7	2·0	2·0
,, 18 ,, ,,	0·35	0·55	0·55

After the hypochlorite solutions had remained for ten days in stoppered flasks, 100 c.c. of the solutions were made up to 500 c.c. with water, and boiled linen (19·7 grams) again introduced:

	Li.	Na.	K.
Original	3·55	3·55	3·55
After 30 mins.	2·6	2·65	2·55
,, 1 hour	2·35	2·4	2·3

The colour of the bleached cloth in all the experiments pointed to the same conclusion as the figures, namely, that the bleaching actions of the three solutions were the same.

Solutions of potassium and sodium hypochlorites were now made from bleaching powder solution by precipitation with solutions of the alkali carbonates, a slight excess of the bleaching powder solution being used in order to ensure against the complications due to an excess of carbonate. Fifty c.c. of the solutions were made up to 500 c.c., and 40·3 grams of linen added. Again titrations of 10 c.c. of the liquors were periodically made to give the table:

	Na.	K.
Original	13·4	13·7
After 30 mins.	8·5	8·7
,, 1 hour	7·2	7·4
,, 1½ hours	4·6	4·8

These figures again show that the solutions have the same bleaching efficiency.

Bleaching Action of the Neutralised Solutions.

One hundred c.c. of each of the three hypochlorites solutions made for the first tests were diluted with water (to a litre of which 1 c.c. of dilute sulphuric acid had been added) to give 500 c.c. of liquor, and in each case 19·7 grams of linen were added, titrations being made as before:

	Li.	Na.	K.
Original	3·4	3·5	3·45
After 30 mins.	2·3	2·35	2·3
,, 1 hour	1·95	2·0	1·95

The solutions were found to be still slightly alkaline to litmus after adding this small amount of sulphuric acid, but the figures show that this quantity of acid has an effect in stimulating the bleaching efficiency (compare with results without acid), and that the effect is practically the same for all three solutions.

Bleaching Actions of the Acidified Solutions.

When made just acid by adding more sulphuric acid in the manner described, the following results were obtained:

	Li.	Na.	K.
Original	1·3	1·3	1·3
After 1 hour	0·3	0·35	0·35
,, 2 hours	0·1	0·1	0·1

The experiments fully prove that in all similar circumstances the hypochlorites of the three metals have identical properties. As previously mentioned, the bleaching properties of the solutions used in the experiments are affected by the presence of the hydroxides and the sulphates of the alkali metals, the bleaching efficiency of the hypochlorite solutions being therefore determined by the efficiencies of the pure hypochlorites stimulated by the presence of the alkali sulphates, and retarded by the presence of the alkali hydroxides. In the case of the tests with the addition of sulphuric acid, however, we have the alkali hydroxides changed into sulphates, so that there is only the action of the sulphates to be considered, and these being present in equivalent proportions in the three cases have identical actions (Higgins, *loc. cit.*). As it was found that the bleaching properties after adding sulphuric acid were still identical, it follows from the above reasoning that the bleaching properties of solutions of the pure hypochlorites are identical, that is, without the presence of either hydroxide or sulphate. In short, if the hypochlorites of the alkali metals could be produced in the pure state, their solutions would have the same bleaching efficiency. These results serve to show that the base to which the hypochlorous acid is joined does not influence the bleaching action. Indeed, it is probable that this holds for all hypochlorite solutions; thus, figures collected from previous experiments (Higgins, *J. Soc. Chem. Ind.*, 1911, **30**, 185) show that calcium hypochlorite solutions are almost identical in bleaching properties with the sodium hypochlorite solutions prepared from them; in fact, the calcium solutions are found to be a little more active because the carbon dioxide of the air precipitates the free lime from them, whereas by the action of the carbon dioxide of the air the free alkali of the sodium hypochlorite solution is changed into sodium carbonate, and remains in solution to retard the bleaching activity of the solution. The insolubility of the calcium carbonate and its consequent removal from solution aiding the hydrolysis of the remaining hypochlorite, is the cause of the slightly increased bleaching efficiency of bleaching powder over sodium hypochlorite prepared from it. If magnesium sulphate is used for precipitating the bleaching powder solution, calcium sulphate is produced from the interaction of the calcium and sulphate ions, and at the same time the free lime contained in the bleaching powder solution reacts with the magnesium sulphate, producing calcium sulphate and insoluble magnesium oxide, so that on filtering the mixture a solution of magnesium hypochlorite is obtained, which contains no free alkali. This solution has, therefore, more active bleaching properties than the solution from which it was made, because there is nothing to retard the hydrolysis of the hypochlorite, and thus hinder the bleaching action. This increased activity, however, has nothing to do with the fact that the base is magnesium and not calcium; if hydroxyl ions could be introduced into the solution, as in the case of the calcium solution, the efficiency would be the same as that of the original bleaching powder solution. The same remarks apply to the production of zinc hypochlorite.

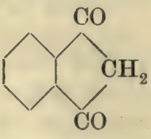
Moreover, it must be remembered that the removal of the free lime from bleaching powder solution by the carbon dioxide of the air is a slow process (Higgins, Trans., 1911, **99**, 858), and it is because of this slow elimination that bleaching powder solution does not differ much in its stability and bleaching efficiency from sodium hypochlorite solution of the same alkalinity. If the free lime be removed very quickly from the bleaching powder solution, then the solution would have a greater bleaching efficiency; in fact, it would be about as active as solutions of magnesium and zinc hypochlorites.

The above experiments point to bleaching being produced by both hypochlorites and hypochlorous acid, but as hypochlorous acid is not so stable as the hypochlorites, and therefore of greater bleaching effect, any alteration, for example, by hydrolysis, which increases the amount of the acid in solution, increases the bleaching efficiency of that solution.

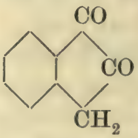
XXVIII.—1 : 2-*Diketohydrindene.*

By William Henry Perkin, jun., Walter Morrell Roberts, and Robert Robinson.

The keto-derivatives of hydrindene have repeatedly been the subject of careful investigation, and yet, although 1 : 3-diketohydrindene (I) is well known (Gabriel and Neumann, *Ber.*, 1893, **26**, 954; Wislicenus, *Annalen*, 1888, **246**, 351; Wislicenus and Kötzle, *Annalen*, 1889, **252**, 72; Kaufmann, *Ber.*, 1897, **30**, 385), the isomeric 1 : 2-diketohydrindene (II) has not so far been described.



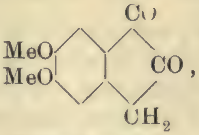
(I.)



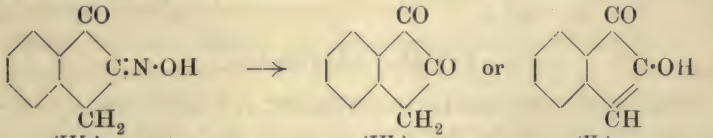
(II.)

There can, however, be no doubt that 1 : 2-diketohydrindene, and especially its dimethoxy- and methylenedioxy-derivatives, might be expected to exhibit interesting properties, and to prove very valuable in the synthesis of alkaloids and other natural products.

It appears to us that the difficult problem of the synthesis of brazilin might very probably be best solved by employing dimethoxy-1 : 2-diketohydrindene:

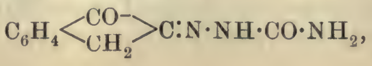


as the starting point. Considerations such as these made it desirable that methods should be available for the preparation of substances of this kind, and we decided, in the first place, to attempt the preparation of 1: 2-diketohydrindene itself by some process which could subsequently be utilised in the synthesis of the dimethoxy- and methylenedioxy-derivatives. After several methods had been tried without success, we ultimately discovered that 1: 2-diketohydrindene may be readily obtained from the *iso*nitroso-*α*-hydrindone (III), first prepared by Kipping (Trans., 1894, **65**, 492) from *α*-hydrindone by treatment with sodium nitrite and acetic acid (compare Gabriel and Stelzner, *Ber.*, 1896, **29**, 2604). When this *iso*nitroso-derivative is hydrolysed by hydrochloric acid, in the presence of formaldehyde, it is readily converted into 1: 2-diketohydrindene:



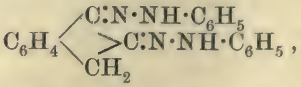
(III.) (IV.) (V.)

the function of the formaldehyde being to combine with the hydroxylamine simultaneously produced, and to remove it from the sphere of action. Whilst 1: 3-diketohydrindene is colourless, the 1: 2-isomeride is, as might be expected from its *o*-diketonic structure, deep yellow; it is probable therefore that the constitution of 1: 2-diketohydrindene is that represented by formula (IV), but, on the other hand, no evidence is available which excludes the constitutional formula (V). When 1: 2-diketohydrindene is treated with hydroxylamine, it is readily converted into the oxime, which melts at 215°, and is identical with *iso*nitroso-*α*-hydrindone, a proof that the carbonyl group in the 2-position reacts more readily with hydroxylamine than that in the 1-position. The semicarbazone, produced in the usual manner, melts at 225°, and has the probable constitution:



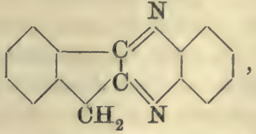
$$C_6H_4{<}{\substack{CO-\\CH_2}}{>}C{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2,$$

and the diketone reacts readily with phenylhydrazine, with formation of the osazone:



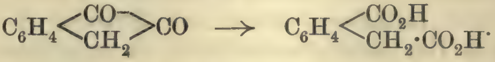
$$C_6H_4\begin{cases} C{:}N\cdot NH\cdot C_6H_5 \\ \quad >C{:}N\cdot NH\cdot C_6H_5 \\ CH_2 \end{cases},$$

which melts at 230—235°, and is identical with the substance which Gabriel (*Ber.*, 1896, **29**, 2603) obtained from *iso*nitroso-*α*-hydrindone by the action of phenylhydrazine. A characteristic derivative of 1:2-diketohydrindene is indenoquinoxaline:



which is produced quantitatively from the diketone by treatment with *o*-phenylenediamine, and melts at 164—165°.

1: 2-Diketohydrindene is readily oxidised by hydrogen peroxide, with formation of homophthalic acid:



$$C_6H_4<\begin{matrix} CO- \\ CH_2 \end{matrix}>CO \longrightarrow C_6H_4<\begin{matrix} CO_2H \\ CH_2\cdot CO_2H \end{matrix}.$$

We are at present engaged in a further study of 1: 2-diketohydrindene and its derivatives.

1: 2-*Diketohydrindene.*

After many comparative experiments, the following process was ultimately adopted for the preparation of this substance.

*iso*Nitroso-*α*-hydrindone (10 grams) is mixed with formaldehyde (35—40 grams of the 40 per cent. aqueous solution), and then concentrated hydrochloric acid gradually added, the mixture being stirred continuously until the precipitate acquires a deep yellow colour.

After collection, the crude diketohydrindene is washed with water, dried, and crystallised from benzene or ether, when beautiful golden-yellow plates are obtained, the yield of pure substance being approximately 85 per cent. of that theoretically possible:

0·1112 gave 0·3015 CO_2 and 0·0407 H_2O. C=73·9; H=4·1.
0·1160 „ 0·3162 CO_2 „ 0·0424 H_2O. C=73·8; H=4·0.
$C_9H_6O_2$ requires C=73·9; H=4·0 per cent.

1: 2-*Diketohydrindene* melts between 95° and 115°, and this behaviour is not altered by repeated crystallisation. It is rather sparingly soluble in non-hydroxylic solvents, but is readily dissolved by chloroform, and the addition of light petroleum to the chloroform solution gives a clear liquid from which the diketone crystallises well. The solutions in non-hydroxylic solvents are deep yellow, but, when the substance is dissolved in methyl or ethyl alcohols, in both of which it is very readily soluble, very pale yellow or nearly colourless solutions are obtained, an indication that the substance has combined with the solvent. The finely divided substance dissolves in boiling water with a deep green colour, and it is also slowly attacked by sodium carbonate, yielding an olive-green solution which becomes greenish-blue on keeping, and very intense blue on boiling; on diluting with water, the colour changes to pale brown.

The behaviour with alkali hydroxide is quite different, since the substance dissolves immediately in 5 per cent. sodium hydroxide to a colourless solution, which rapidly becomes brownish-red, and then brownish-yellow, and on acidifying, a colourless, flocculent precipitate is produced. When the alkaline liquid is boiled, the colour changes are through violet to dull red. If, however, the substance is boiled with a trace only of alkali, the colour changes are similar to those produced in the case of sodium carbonate. The solution of the substance in sulphuric acid is pale yellow, and, when mixed with indole-*α*-carboxylic acid, becomes blood-red. A similar blood-red solution is also produced by shaking the diketone in sulphuric acid with benzene containing thiophen, but in this case the colour changes to greenish-brown in a few minutes. These reactions are very similar to those produced by isatin under the same conditions, and are therefore probably due to condensations in which one of the keto-groups are involved. In presence of hydrochloric acid, the diketone condenses with resorcinol, but, although the product is colourless and solid, it has not been obtained in a sufficiently pure condition to give consistent analytical results.

The *oxime* (*iso*nitroso-*α*-hydrindone) is obtained when 1:2-diketohydrindene, dissolved in methyl alcohol, is treated with excess of solution of hydroxylamine hydrochloride and sodium acetate. On gently warming, the oxime is precipitated, and is collected and recrystallised from benzene. Examination showed that the substance is identical with *iso*nitroso-*α*-hydrindone; it shrinks at 200°, and melts at 215°, and these properties are unaltered by admixture with an equal amount of *iso*nitroso-*α*-hydrindone.

The *Semicarbazone*.—This derivative, which is doubtless analogously constituted to the oxime, may be prepared by the action of semicarbazide acetate on the diketone at the ordinary temperature in the usual manner. It crystallises from methyl or ethyl alcohols in colourless, feathery needles, which darken at 225°, and melt and decompose at 230—233°:

0·1079 gave 0·2317 CO_2 and 0·0443 H_2O. C=58·6; H=4·6.
0·0721 „ 13·1 c.c. N_2 at 23° and 752 mm. N=20·8.
$C_{10}H_9O_2N_3$ requires C=59·1; H=4·4; N=20·7 per cent.

On boiling with hydrochloric acid, the semicarbazone is readily decomposed with regeneration of 1:2-diketohydrindene.

The *Dihydrazone* or *Osazone*.—This substance had been previously prepared by Gabriel (*Ber.*, 1896, **29**, 2603) by the action of phenylhydrazine on *iso*nitroso-α-hydrindone. It is readily obtained by warming diketohydrindone with excess of phenylhydrazine in acetic acid solution. It melts at 230—235°, and the melting point is not changed by admixture with a specimen of the substance prepared by Gabriel's method (Found, N=17·2; $C_{21}H_{18}N_4$ requires N=17·2 per cent.).

Indenoquinoxaline.—This quinoxaline derivative separates quantitatively in a few seconds when concentrated methyl-alcoholic solutions of equimolecular proportions of 1:2-diketohydrindene and *o*-phenylenediamine are mixed in the cold. It is purified by crystallisation from methyl alcohol, and is thus obtained in slender, colourless needes, melting at 164—165°:

0·1231 gave 0·3726 CO_2 and 0·0489 H_2O. C=82·6; H=4·4.
$C_{15}H_{10}N_2$ requires C=82·6; H=4·6 per cent.

Indenoquinoxaline does not exhibit fluorescence even in benzene solution. When dissolved in sulphuric acid, it yields a clear yellow solution, from which the original colourless substance is precipitated by water. It combines with concentrated hydrochloric acid to form a yellow salt, and, when this is suspended in acetic acid and treated with a trace of ferric chloride, it quickly dissolves, and in a short time the ferrichloride of the base separates as a yellow powder, consisting of micro-prisms. The *picrate* is readily obtained as a voluminous mass of feathery needles, melting at 176—177°, when picric acid and indenoquinoxaline are dissolved together in hot ethyl alcohol, and the solution allowed to cool slowly:

0·1157 gave 15·6 c.c. N_2 at 20° and 760 mm. N=15·7.
$C_{15}H_{10}N_2,C_6H_3O_7N_3$ requires N=15·7 per cent.

Oxidation of 1:2-diketohydrindene to Homophthalic Acid.—In carrying out this oxidation, 1:2-diketohydrindene, dissolved in methyl alcohol, was treated with excess of hydrogen peroxide (30 per cent.), and one or two drops of concentrated hydrochloric acid. The liquid was evaporated to dryness on the steam-bath, and the residue recrystallised from water. The acid thus obtained in very good yield melted at 175—176°, and was identical with homophthalic acid (Found, C=59·8; H=4·7. Calc., C=60·0; H=4·4 per cent.).

The authors take this opportunity of stating that the cost of these experiments has been largely defrayed by a grant from the Research Fund of the Chemical Society.

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XXIX.—*The Esterification Constants of some Substituted Acetic and Benzoic Acids.*

By JOHN JOSEPH SUDBOROUGH and MARGARET KATHLEEN TURNER.

IN an earlier paper (Sudborough and Lloyd, Trans., 1899, **75**, 467) the esterification constants of a number of substituted acetic acids were given. These were obtained by using ethyl alcohol with hydrogen chloride as catalyst. The alcohol contained small amounts of water, as it had not been distilled over calcium, and some difficulty was experienced in keeping the temperature constant.

We have determined the constants for a number of the same acids, using methyl alcohol, which has been distilled five times over small amounts of metallic calcium (compare Gyr, *Ber.*, 1908, **41**, 4322). In addition, we have examined the rates of esterification of some ortho-substituted benzoic acids by the catalytic method. A few of these acids had been already examined by Goldschmidt (*Ber.*, 1895, **28**, 3218; *Zeitsch. Elektrochem.*, 1909, **15**, 4).

Our main object in carrying out these determinations was to ascertain whether a given substituent when introduced into the ortho-position in the benzoic acid molecule has the same relative retarding effect on catalytic esterification as when introduced into the α-position in the acetic acid molecule.

The catalytic method of esterification was adopted, using pure methyl alcohol with hydrogen chloride as catalyst. The general method was similar to that already described (Trans., 1899, **75**, 471; 1909, **95**, 318), except that the mixture of organic acid and catalyst solutions was not divided and placed in several small bottles, but was kept in a single vessel in the thermostat, and portions of this solution were withdrawn by means of a pipette for titration after given intervals of time. In the great majority of cases the titrations were made with standard barium hydroxide, using phenolphthalein as indicator; but very strong acids of the type of the chloroacetic acids were titrated with ammonium hydroxide solution, using litmus as indicator. This procedure is necessary, as the esters of these strong acids are so readily hydrolysed by barium hydroxide solution that a definite, sharp end-point cannot be obtained with this alkali.

The following results have been obtained:

Acid.	Temp.	Series.	No. of titrations.	Concentration of hydrogen chloride.	$1/t \log_{10} a/a-x$.			$\Sigma^{15^\circ}_{\mathrm{MeOH}}$.	$\Sigma^{20^\circ}_{\mathrm{MeOH}}$.
					Min.	Max.	Mean corrected for *N*-HCl.		
Phenylacetic	15°	*a*	8	0·01048*N*	0·229	0·256	23·00	53·80	—
	15	*b*	8	0·00967	0·212	0·233	23·06		
	20	*a*	8	0·00936	0·278	0·299	30·98	—	71·1
	20	*b*	7	0·00950	0·284	0·297	30·53		
	20	*c*	8	0·01003	0·299	0·340	31·11		
Chloroacetic	15	*a*	6	0·00951	0·147	0·163	16·09	37·0	—
	15	*b*	7	0·00946	0·146	0·160	16·06		
	20	*a*	7	0·01410	0·317	0·375	24·96	—	56·2
	20	*b*	8	0·00965	0·205	0·266	23·83		
Bromoacetic	15	*a*	8	0·01006	0·155	0·181	16·70	38·7	—
	15	*b*	6	0·00987	0·162	0·174	16·93		
Iodoacetic	15	*a*	8	0·00956	0·117	0·133	13·18	30·4	—
	15	*b*	8	0·00956	0·116	0·134	13·18		
Cyanoacetic	15	*a*	6	0·01305	0·0188	0·0198	1·48	3·4	—
	15	*b*	6	0·01305	0·0189	0·0209	1·49		
Phenoxyacetic	15	*a*	7	0·00763	0·128	0·135	17·3	40·1	—
	15	*b*	8	0·00903	0·147	0·178	17·6		
	15	*c*	8	0·00905	0·148	0·167	17·35		
Dichloroacetic	20	*a*	7	0·03137	0·0801	0·0891	2·70	—	6·29
	20	*b*	7	0·02193	0·0565	0·0706	2·76		
Trichloroacetic	15	*a*	4	0·00967	0·00327	0·00420	0·406	0·969	—
	15	*b*	5	0·00967	0·00333	0·00450	0·435		
Nitroacetic *	15	*a*	1	0·01053	—	0·0422	4·01	—	—
	15	*b*	1	0·01330	—	0·0437	3·29		
Benzoic	15	*a*	8	0·04888	0·00540	0·00771	0·122	0·283	—
	15	*b*	7	0·01824	0·00213	0·00242	0·124		
	15	*c*	7	0·01834	0·00217	0·00235	0·123		
	20	*a*	7	0·04360	0·00794	0·00892	0·191	—	0·437
	20	*b*	8	0·02576	0·00465	0·00509	0·189		
o-Toluic	15	*a*	7	0·01270	0·000466	0·000565	0·0398	0·092	—
	15	*b*	8	0·04501	0·00173	0·00193	0·0400		
o-Ethylbenzoic	15	*a*	8	0·04733	0·00105	0·00124	0·0243	0·056	—
	15	*b*	7	0·04345	0·00101	0·00109	0·0244		
	20	*a*	6	0·05050	0·00199	0·00208	0·0402	—	0·092
	20	*b*	6	0·03111	0·00121	0·00127	0·0399		
o-Propylbenzoic	15	*a*	8	0·04733	0·000946	0·00102	0·210	0·049	—
	15	*b*	8	0·04345	0·000883	0·00105	0·218		
Diphenyl-1-carboxylic	15	*a*	6	0·4888	0·00105	0·00119	0·0223	0·051	—
	15	*b*	6	0·4630	0·00983	0·00104	0·0218		
o-Salicylic	15	*a*	4	0·02876	0·000144	0·000180	0·00560	0·0129	—
	20	*a*	7	0·04637	0·000448	0·000462	0·00983	—	0·0235
	20	*b*	7	0·01450	0·000148	0·000168	0·01055		
o-Phenoxybenzoic	15	*a*	7	0·01289	0·00256	0·00275	0·2056	0·471	—
	15	*b*	8	0·02881	0·00555	0·00631	0·2031		
Acetophenone-*o*-carboxylic	15	*a*	6	0·02775	0·0906	0·0988	3·39	7·69	—
	15	*b*	7	0·01633	0·0515	0·0558	3·29		

* As nitroacetic acid decomposes slowly in presence of water, one titration only was made after the mixture had remained for a short time. Even then, difficulties were met with in determining the end-point of the titration, using ammonia with litmus as indicator.

Acid.	Temp.	Series.	No. of titrations.	Concentration of hydrogen chloride.	$1/t \log_{10} a/a-x$.				
					Min.	Max.	Mean corrected for N-HCl.	$\Sigma^{15^\circ}_{\mathrm{MeOH}}$.	$\Sigma^{20^\circ}_{\mathrm{MeOH}}$.
o-Chlorobenzoic	15	*a*	6	0·02616	0·00117	0·00124	0·0463	0·105	—
	15	*b*	6	0·04501	0·00192	0·00208	0·0451		
o-Bromobenzoic	15	*a*	6	0·02551	0·000886	0·00101	0·0370	0·085	—
	20	*a*	8	0·02576	0·00127	0·00150	0·0536	—	0·123
o-Iodobenzoic	15	*a*	5	0·02556	0·000660	0·000828	0·0282	0·0625	—
	15	*b*	6	0·05095	0·00131	0·00138	0·0261		
	20	*a*	7	0·05050	0·00199	0·00225	0·0408	—	0·0936
	20	*b*	5	0·03111	0·00123	0·00131	0·0405		
o-Nitrobenzoic	15	*a*	3	0·03094	0·000107	0·000130	0·00381	0·0088	—
	15	*b*	5	0·06730	0·000245	0·000263	0·00380		
o-Benzoyl-benzoic	20	*a*	7	0·01450	0·00144	0·00167	0·106	—	0·244
	20	*b*	6	0·02294	0·00233	0·00258	0·108		
	20	*c*	6	0·03215	0·00322	0·00343	0·104		
o-Naphthoyl-benzoic	20	*a*	7	0·03721	0·00133	0·00148	0·0374	—	0·0897
	20	*b*	8	0·03851	0·00146	0·00171	0·0405		

(1) These results confirm the conclusion previously drawn that substituents in the acetic acid molecule have a retarding effect. The relative effects, however, are not quite the same as those obtained with ethyl alcohol; thus both the chloro- and bromo-acetic acids are esterified less readily than acetic acid, and the bromo- somewhat more readily than the chloro-acid. The order of diminishing reactivity given previously was CH_3, Cl, C_6H_5, Br, I.

The order now obtained for phenyl- and chloro-acetic acids agrees with Gyr's results (*loc. cit.*).

(2) The cyano-group in the case of the acetic acid series appears to have a pronounced inhibiting effect, whereas preliminary experiments tend to show that this is not so in the case of *o*-cyanobenzoic acid.

(3) The results show clearly that dichloroacetic acid is esterified less readily than the monochloro-acid, and that the trichloro-acid is esterified even more slowly.

(4) The influence of ortho-alkyl substituents in the benzene molecule is marked. The methyl group has the least effect, and the influence of ethyl, *n*-propyl, and phenyl groups in the *o*-position is very similar.

Somewhat the same generalisations hold good in the case of the acetic acid series (Sudborough and Gittins, Trans., 1908, **93**, 211).

(5) The halogen substituents also have a retarding effect in the benzoic series, but the effect is not so marked as that of an ethyl or phenyl group, and their relative order is chlorine, bromine, iodine.

These results are somewhat different from those met with in the aliphatic series of acids.

(6) The most interesting results obtained are those with aceto-

phenone-*o*-carboxylic acid and *o*-phenoxybenzoic acid. Both these acids are esterified more readily than benzoic acid itself by the catalytic method. The ratio benzoic/acetophenone-*o*-carboxylic is about 1/27. So far, these appear to be the only ortho-substituted benzoic acids which are esterified more rapidly than benzoic. *o*-Benzoylbenzoic acid is also esterified fairly quickly, but not so rapidly as benzoic acid. In this connexion it may be pointed out that Graebe (*Ber.*, 1900, **33**, 2026) has shown that 3:6-dichloro- and tetrachloro-benzoylbenzoic acid can be esterified by the catalytic method, although both acids are diortho-substituted.

We are carrying out experiments with the two acids—acetophenone-*o*-carboxylic and *o*-phenoxybenzoic—in order to prove that the neutral products formed by the action of alcohol and hydrogen chloride are esters, and also to determine whether the esters themselves can be readily hydrolysed by acids and alkalis.

Although an acetyl group in the ortho-position has an accelerating effect in the case of benzoic acid, it does not appear to have the same effect when introduced into the molecule of an aliphatic acid.

(7) Dry hydrogen fluoride has been used as a catalyst. Preliminary experiments showed that a solution of hydrogen fluoride in methyl alcohol had not deteriorated after remaining for two days at the ordinary temperature.

The following results were obtained for phenylacetic acid at 15°, concentration of H.F. 0·0447*N*:

t in hours.	$a-x$.	$1/t \log a/a-x$.
0·0	12·62	—
17·7	7·92	0·0114
25·8	6·35	0·0116
41·7	3·80	0·0125
67·0	1·42	0·0141

$$\Sigma^{15^\circ}_{\mathrm{MeOH}} = 0{\cdot}639$$

as compared with $\Sigma^{15^\circ}_{\mathrm{MeOH}}$ 53 when hydrogen chloride is used as catalyst.

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XXX.—*The Influence of Solvents on the Rotation of Optically Active Compounds. Part XVII. The Relationship between the Chemical Constitution and the Influence of a Solvent.*

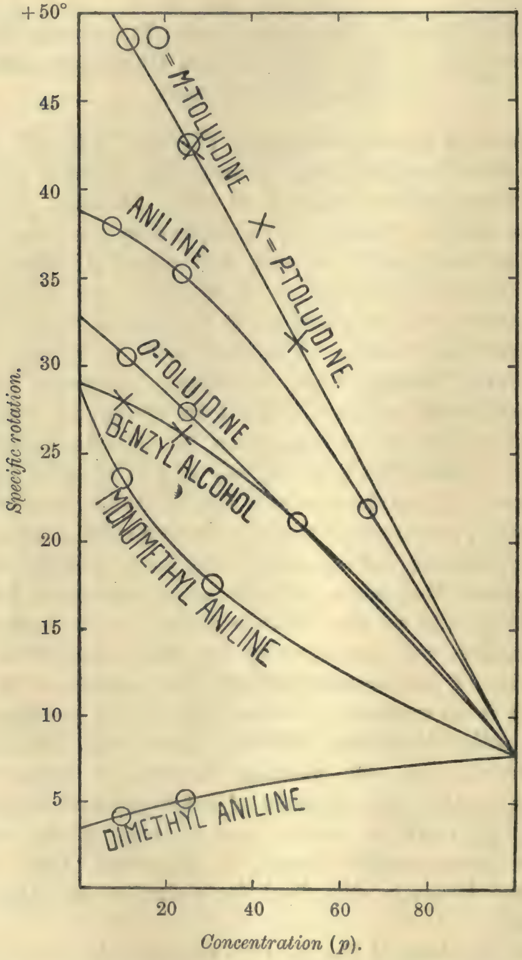
By THOMAS STEWART PATTERSON and ELIZABETH FINDLAY STEVENSON, M.A., B.Sc., late Robert Donaldson Scholar of Glasgow University.

IN the last part of this investigation (Trans., 1910, **97**, 2110) we attempted to trace a relationship between the chemical constitution and the influence on the rotation of ethyl tartrate, of a number of compounds such as phenol, the nitrophenols, the ethers of these substances, the polyhydric phenols, and other solvents. It was pointed out that the change of rotation of the dissolved ester appears to afford a more pronounced indication of constitutional difference than any other criterion, such as refractive index, molecular volume, boiling point, absorption spectrum, etc., which has been used for the purpose. We have thought it worth while, therefore, to extend the investigation to include aniline, monomethylaniline, dimethylaniline; *o*-, *m*-, and *p*-nitroaniline; *o*-, *m*-, and *p*-toluidine; diphenylamine and methyldiphenylamine; as well as benzyl alcohol, phenylethyl alcohol, phenylpropyl alcohol; phenyl acetate, benzyl acetate; benzyl ethyl ether and dibenzyl ether.

We were afraid that some of these basic substances like aniline might act chemically on the ethyl tartrate, but at moderate temperatures this does not appear to be the case, since, after heating, the rotation is not permanently altered, but returns to its original value. There is no evidence to show that, at 20°, solution of ethyl tartrate in aniline is of any different kind from solution in, for example, nitrobenzene. On heating, however, to higher temperatures, say, above 100°, the solution of ethyl tartrate in these basic solvents becomes dark in colour, and on cooling the rotation is found to be permanently altered, a behaviour thus somewhat similar to that formerly described for quinoline solutions (Trans., 1909, **95**, 325).

Our results for those of the solvents mentioned, which were most completely examined, are shown in the diagram, which exhibits the relationship between concentration and specific rotation at 20°. It will be seen that aniline has a very marked effect, causing the rotation to rise from +7·66°, the value for the pure ester, to +48·8° at infinite dilution. The substitution of one of the aminic hydrogen atoms by a methyl group diminishes the solvent effect. A $p=10$ solution in aniline has $[\alpha]^{20}_{\mathrm{D}}+37{\cdot}7^\circ$, whilst the specific rotation of a solution of equal percentage composition in methylaniline has only the value $+23{\cdot}65^\circ$, a diminution of 14·05°. The introduction of a second methyl group has a similar but greater

Ethyl tartrate in various solvents. Concentration–rotation curves.



effect, lowering the rotation to $+4{\cdot}2^\circ$, or by 19·45°. Dimethylaniline has, therefore, a depressing influence on the rotation of ethyl tartrate. It is remarkable that the shape of the curve for monomethylaniline is different from that of the aniline and dimethylaniline curves.

We may compare with these the data for diphenylamine and methyldiphenylamine, but here, owing to the comparatively slight solubility of the former, it was necessary to compare the effects for much stronger solutions.* It might be supposed that since aniline has a powerful elevating effect on the rotation of the tartrate, and methylaniline one less powerful, that diphenylamine should have a greater influence even than aniline.

TABLE I.

Solvent.	*p*.	a^{20}_{D} [100 mm.]
Aniline	66·29	+16·5°
Diphenylamine	66·85	10·35
Methyldiphenylamine	69·67	6·35

As will be seen from the table above, however, this expectation is not realised. A phenyl group introduced into aniline brings about a diminution of solvent influence, whilst the further introduction of a methyl group causes another and greater reduction.

Returning to the diagram, it will be noticed that when a methyl group, instead of being substituted in the amino-radicle of aniline, is introduced into the ring, the changes produced in the solvent influence of the resulting compound are again quite considerable. In *o*-toluidine, at infinite dilution, the rotation is lower than in aniline by some 6°, but in *m*- and *p*-toluidine, in which two solvents the rotation appears to be the same, it is higher by 14·2°. With these results we may compare those for the nitroanilines, which again, on account of the solubility relationships, could only be examined in very concentrated solutions.

TABLE II.

Solvent.	*p*.	a^{20}_{D} [100 mm.].
Aniline	90	+12·85°
o-Nitroaniline	89·3	12·05
m-Nitroaniline	89·43	11·83
p-Nitroaniline	90·02	17·77

The introduction of an *o*-nitro-group into aniline slightly depresses the solvent influence; a *m*-nitro-group has a somewhat greater depressing effect, but a *p*-nitro-group brings about a very pronounced rise. The relationship of *o*-, *m*-, and *p*-isomerism to solvent effect has already been referred to in various parts of this investigation, and in the following table there are collected together the results hitherto obtained in regard to this point.

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* The strength of a solution is always expressed as grams of ethyl tartrate per 100 grams of solution.

TABLE III.

The ortho-derivatives have a greater solvent influence than the para-derivatives when the substituting groups are:

CH_3	CH_3	(Trans., 1902, **81**, 1107)	NO_2	$O{\cdot}CH_3$	(Trans., 1910, **97**, 2114)
CH_3	NO_2	,, 1908, **93**, 1841	NO_2	$O{\cdot}C_2H_5$	,, ,, ,, ,,
NO_2	NO_2	,, ,, ,, ,,	NO_2	Cl	,, ,, ,, ,,

and α-nitronaphthalene, which may be regarded as an ortho-derivative, has a greater solvent effect than β-nitronaphthalene, a meta-derivative (Trans., 1908, **93**, 1842).

The para-derivatives have a greater solvent influence than the ortho-derivatives when the substituting groups are:

NO_2	OH	(Trans., 1910, **97**, 2118)	CH_3	NH_2
OH	OH	,, ,, ,, ,,	NO_2	NH_2

whilst β-naphthol, a meta-derivative, has a greater influence than α-naphthol, an ortho-derivative (Trans., 1910, **97**, 2120).

Passing now to the other data obtained in this investigation, we may quote these figures:

TABLE IV.

Solvent.	*p*.	α_D^{20}.	Solvent.	*p*.	α_D^{20}.
Phenol	23·85	+9·0°	Benzyl alcohol ...	23·38	+6·634°
Phenyl acetate	24·96	5·28	Benzyl acetate ...	24·89	4·68

Thus the effect of replacing the typical atom of phenol or of benzyl alcohol by an acetyl group is to diminish considerably the solvent influence of the resulting compound, and this is very similar to what has already been recorded for the replacement of the hydroxylic hydrogen atom of phenol by a methyl or an ethyl group to form the ethers of phenol, but the effect in the present case is not so marked. This is seen further from the figures in the following table:

TABLE V.

Solvent.	*p*.	α_D^{20}.	Solvent.	*p*.	α_D^{20}.
Phenol *	23·85	+9·0°	Benzyl alcohol ...	23·38	+6·634°
Diphenyl ether *	24·58	1·95	Dibenzyl ether ...	24·84	3·07
			Benzyl ethyl ether	20·78	2·26

* Trans., 1910, **97**, 2124, 2126.

As was shown in our last paper, diphenyl ether has a much less effect than phenol, and it now appears that an analogous relationship obtains between dibenzyl ether and benzyl alcohol. Benzyl ethyl ether has a rather less influence than dibenzyl ether.

One other comparison is given in table VI.

TABLE VI.

Solvent.	p.	α_D^{20}.	Solvent.	p.	α_D^{20}.
Phenol	23·85	+9·0°	β-Phenylethyl alcohol	26·3	+4·48°
Benzyl alcohol	23·38	6·634	γ-Phenylpropyl alcohol	24·83	3·63

The introduction of a CH_2-group between the C_6H_5-group and the OH-group of phenol, so as to produce benzyl alcohol, diminishes the solvent influence considerably. The repetition of this process to give phenylethyl alcohol is accompanied by a further diminution of solvent influence by a somewhat less amount, whilst the introduction of a third CH_2-group, yielding γ-phenylpropyl alcohol, is accompanied by results of a closely analogous character. This behaviour is very similar to that which was formerly observed in the series of aliphatic alcohols (Trans., 1901, **79**, 180, 483).

Little need be said about the effect of temperature change on the rotation of these solutions, as it is just what has almost invariably been found for other solutions of ethyl tartrate. When the specific rotation of the solution is about 20° or above it, the rotation diminishes with rise of temperature; otherwise it increases. This point can be examined more closely, if that should be desired, from the experimental data which follow, in regard to which it may be remarked that only interpolated values are given for the densities of the solutions; from them, however, the density-temperature curves can just as readily be reproduced as from the actual experimental figures. All interpolated numbers in the tables are printed in italics.

EXPERIMENTAL.

The solvents were all distilled under diminished pressure before use.

Aniline.—Density of aniline used.

t	15·1°	*20°*	20·6°	25·1°
d	1·0262	*1·0221*	1·0215	1·0176

$p = 7·66$:

t	17·2°	*20°*	34·7°	59·3°	70·7
d	1·0373	*1·0346*	1·0217	1·0002	0·9903
α_D^t	+3·027	*2·984*	2·854	2·623	2·528
$[\alpha]_D^t$	+38·10	*37·66*	36·47	34·23	33·33

$p = 23·98$:

t	14·6°	*20°*	38·1°	55·6°	81·8°	12·7°*
d	1·0681	*1·0630*	1·0468	1·0305	1·0068	1·070
α_D^t	+9·206	*8·986*	8·402	7·709	7·107	9·309
$[\alpha]_D^t$	+36·08	*35·25*	33·56	31·28	29·51	36·38

* After cooling.

Aniline (continued).

$p = 66·29$:

t	12·6°	*20°*	43·2°	75·2°	86·1°	12·2° *
d...	1·1472	*1·1400*	1·1182	1·0872	1·0767	1·1475
α^t_D	+16·775	*16·5*	15·787	14·957	14·712	16·81
$[\alpha]^t_D$	+22·05	*21·823*	21·3	20·75	20·61	22·10

* After cooling.

Monomethylaniline.

$p = 9·936$:

t	14·9°	*20°*	31·7°	49·8°	65°
d	1·0069	*1·0036*	0·9938	0·9787	0·9662
α^t_D	+2·388	*2·358*	2·280	2·220	2·156
$[\alpha]^t_D$	+23·87	*23·65*	23·09	22·83	22·46

$p = 30·89$:

t	*20°*	19·4°	15·7°	15·3°
d	*1·0445*	1·0450	1·0481	1·0486
α^t_D	*5·672*	5·658	5·608	5·596
$[\alpha]^t_D$	*17·58*	17·53	17·32	17·28

Dimethylaniline.

$p = 9·4$:

t	16·4°	*20°*	26·6°	43°	33·9°	19·3 *
d...........	0·9774	*0·9744*	0·9687	0·9548	0·9625	0·975
α^t_D	+0·282	*0·385*	0·514	0·697	0·595	0·342
$[\alpha]^t_D$	+3·07	*4·2*	5·65	7·68	6·58	3·73

* After cooling.

$p = 24·84$:

t	15·6°	*20°*	30·9°	47·3°	50·9°
d	1·0100	*1·0061*	0·9963	0·9816	0·9785
α^t_D	+1·145	*1·287*	1·632	2·073	2·286
$[\alpha]^t_D$	+4·56	*5·15*	6·60	8·50	9·41

Diphenylamine.

$p = 66·85$:

t.....................	16·3°	*20°*	22·1°	29·2°	31·3°	44·6°
α^t_D	+10·02	*10·35*	10·5	10·91	11·01	11·45

Methyldiphenylamine.

$p = 69·67$:

t	13·9°	*20°*	22·9°	30·5°	40·5°
α^t_D	+6·06	*6·35*	6·39	7·28	8·02

$p = 90·09$:

t	16·7°	*20°*	26·5°	33·4°	39°
α^t_D	+8·15	*8·32*	3·74	9·41	10·29

o-*Toluidine.*

$p=10·93$:

t	12·6°	*20°*	38·2°	47·4°	28·9° *
d	1·0250	*1·0187*	1·0031	0·9954	1·0111
α^t_D	+3·5	*3·397*	3·22	3·084	3·248
$[\alpha]^t_D$	+31·25	*30·5*	29·37	28·33	29·40

$p=25·096$:

t	15°.	*20°*	45·7°	58°	29·4° *
d	1·0502	*1·0457*	1·0228	1·0120	1·0373
α^t_D	+7·331	*7·19*	6·586	6·407	6·974
$[\alpha]^t_D$	+27·82	*27·4*	25·66	25·23	26·79

$p=50·3$:

t	14·9°	*20°*	34·6°	50·5°
d	1·1007	*1·0960*	1·0825	1·0677
α^t_D	+11·758	*11·63*	11·265	10·946
$[\alpha]^t_D$	+21·24	*21·1*	20·69	20 38

* After cooling.

m-*Toluidine.*

$p=11·659$:

t	15·5°	*20°*	29·7°	43·2°
d	1·0154	*1·0117*	1·0033	0·9920
α^t_D	+5·857	*5·721*	5·397	4·932
$[\alpha]^t_D$	+49·47	*48·50*	46·13	42·16

$p=24·964$:

t	16·3°	*20°*	32·9	48°	64·3°
d	1·0407	*1·0376*	1·0267	1·0140	1·0005
α^t_D	+11·276	*10·982*	10·09	9·208	8·34
$[\alpha]^t_D$	+43·3	*42·4*	39·37	36·39	33·39

p-*Toluidine.*

$p=24·925$:

t	*20°*	35·7°	46·8°	57·7°	67·8°
d	*1·035*	1·0217	1·0126	1·0035	0·995
α^t_D	+*10·924*	10·048	9·514	8·846	8·33
$[\alpha]^t_D$	+*42·35*	39·45	37·70	35·37	33·59

$p=49·98$:

t	16·8°	*20°*	34·7°	46·3°	58·2°
d	1·0920	*1·0890*	1·0755	1·0647	1·0537
α^t_D	+17·32	*17·09*	16·02	15·20	14·474
$[\alpha]^t_D$	+31·73	*31·4*	29·80	28·63	27·48

o-*Nitroaniline.*

$p=89{\cdot}3$:

t	14·4°	*20°*	21·7°	31·4°	38·6°
α_D^t	+11·635	*12·05*	12·21	12·81	13·49

m-*Nitroaniline.*

$p=89{\cdot}43$:

t	*20°*	36·6°	48·6°	14·4° *	26·8° *
α_D^t	*+11·83*	13·06	13·84	11·47	12·19

* After cooling.

p-*Nitroaniline.*

$p=90{\cdot}02$:

t	16·3	*20°*	22·6°	34·8°	41·6°	52·4°
α_D^t	+17·795	*17·77*	17·73	17·965	18·205	18·375

Benzyl Alcohol.

$p=10$:

t	17°	*20°*	46·9°
d	1·0636	*1·0613*	1·0408
α_D^t	+2·998	*2·972*	2·718
$[\alpha]_D^t$	+28·19	*28·0*	26·11

$p=23{\cdot}38$:

t	*20°*	21·4°	45·1°	75·6°	101·1°
d	*1·0819*	1·0825	1·062	1·0362	1·0143
α_D^t	*+6·634*	6·624	6·246	5·778	5·443
$[\alpha]_D^t$	*+26·23*	26·17	25·16	23·85	22·95

Benzyl Acetate.

$p=24{\cdot}89$:

t	16·3°	*20°*	31·8°	43·7°	51·7°
α_D^t	+4·63	*4·68*	4·72	4·75	4·815

Phenyl Acetate.

$p=24{\cdot}96$:

t	*20°*	22·6°	28·2°	39·3°	44·4°
α_D^t	*+5·28*	5·29	5·325	5·395	5·365

Benzyl Ethyl Ether.

$p=20{\cdot}78$:

t	13°	*20°*	26·5°	36·3°	42·5°
α_D^t	+2·175	*2·26*	2·39	2·57	2·825

Dibenzyl Ether.

$p=24{\cdot}84$:

t	16·4°	*20°*	27·6°	32·2°	40·9°
α_D^t	+2·995	*3·07*	3·205	3·35	3·535

β-Phenylethyl Alcohol.

$p = 26{\cdot}3$:

t	*20°*	40·7°	27·8°	17·1°	33°	43·1°
α^t_D	*+4·48*	4·545	4·52	4·495	4·525	4·61

γ-Phenylpropyl Alcohol.

$p = 24{\cdot}83$:

t	16·2°	*20°.*	28·7°	38·2°	42°
α^t_D	+3·59	*3·63*	3·73	3·815	3·865

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XXXI.—*The Formation and Reactions of Imino-compounds. Part XVII. The Alkylation of Imino-compounds.*

By JOCELYN FIELD THORPE.

IN Part XIII. of this series (Trans., 1910, **97**, 1299) it was shown that the typical imino-compound, ethyl α-imino-β-cyanoglutarate (I), yields with sodium ethoxide and methyl iodide, first, the monomethyl derivative (II), and then, by further action, a mixture of the two dimethyl derivatives (III and IV):

$$\begin{tikzcd}
 & \underset{\text{(I.)}}{\mathrm{CO_2Et{\cdot}C(CN){:}C(NH_2){\cdot}CH_2{\cdot}CO_2Et}} \arrow[dl] \\
\underset{\text{(II.)}}{\mathrm{CO_2Et{\cdot}C(CN){:}C(NH_2){\cdot}CHMe{\cdot}CO_2Et}} \arrow[r] \arrow[d] & \underset{\text{(III.)}}{\mathrm{CO_2Et{\cdot}C(CN){:}C(NH_2){\cdot}CMe_2{\cdot}CO_2Et}} \\
\underset{\text{(IV.)}}{\mathrm{CO_2Et{\cdot}CMe(CN){\cdot}C(NH_2){:}CMe{\cdot}CO_2Et}} &
\end{tikzcd}$$

Attention was drawn to the similarity in the behaviour of this imino-compound and ethyl glutaconate, a likeness which is still further increased when it is remembered that, according to Blaise (*Bull. Soc. chim.*, 1903, [iii], **29**, 1016), ethyl glutaconate also yields a mixture of the two dimethyl derivatives (V and VI) under similar conditions:

$$\begin{tikzcd}
 & \mathrm{CO_2Et{\cdot}CH{\cdot}CH(H){\cdot}CH{\cdot}CO_2Et} \arrow[dl] \arrow[dr] & \\
\underset{\text{(V.)}}{\mathrm{CO_2Et{\cdot}CMe_2{\cdot}CH{:}CH{\cdot}CO_2Et}} & & \underset{\text{(VI.)}}{\mathrm{CO_2Et{\cdot}CMe{\cdot}CH(H){\cdot}CMe{\cdot}CO_2Et}}
\end{tikzcd}$$

There is, however, one important difference between the two types which suggests a generalisation by which the behaviour of any compound containing the complex $X{\cdot}C{:}C{\cdot}CX$ towards sodium ethoxide and an alkyl iodide can be foretold; thus, whereas ethyl carbethoxymethylglutaconate (VII) reacts with sodium ethoxide, yielding the sodium compound (VIII) (Trans., 1911, **99**, 2191), ethyl β-imino-α-cyanoglutarate gives, as already mentioned, the sodium derivative (IX):

$(CO_2Et)_2C{:}CH{\cdot}CHMe{\cdot}CO_2Et$ (VII.) $CO_2Et{\cdot}C(CN){:}C(NH_2){\cdot}CH_2{\cdot}CO_2Et$ (I.)

$(CO_2Et)_2CNa{\cdot}CH{:}CMe{\cdot}CO_2Et$ (VIII.) $CO_2Et{\cdot}C(CN){:}C(NH_2){\cdot}CHNa{\cdot}CO_2Et$ (IX.)

The conclusion to be derived from this fact may be stated in the following way: *Compounds containing the complex*

$$(X)_2C{:}CR{\cdot}CH_2X,$$

in which X *may be any negative group and* R *any univalent radicle or group, react with sodium ethoxide so as to retain the mobile hydrogen atom, and therefore yield sodium derivatives of the type* $(X)_2C{:}CR{\cdot}C\overset{*}{H}NaX$, *in which the mobile hydrogen atom is represented by* (*). *The replacement of the sodium in this compound by an alkyl group yields the alkyl derivative,* $(X)_2C{:}CR{\cdot}CH(Alk)X$, *and the action of sodium ethoxide on this substance causes the replacement of the mobile hydrogen atom, but the metal then takes up the most negative position in the system, yielding the sodium derivative,* $(X)_2CNa{\cdot}CR{:}C(Alk)X$.

Actually, the swing of the mobile hydrogen atom causes, in certain cases, the formation of the sodium compound,

$$(X)_2C{:}CR{\cdot}CNa(Alk)X,$$

but only to a very small extent. This is shown by the behaviour of both ethyl β-imino-α-cyano-α'-methylglutarate and ethyl methylglutaconate, although it is evident that the tendency to form the last-named sodium derivative must be considerably greater with ethyl methylglutaconate than with the imino-compound, because the former has no distinctively negative position within its system.

In view of the fact that ethyl carbethoxymethylglutaconate reacted with sodium ethoxide, giving the sodium derivative,

$$(CO_2Et)_2CNa{\cdot}CH{:}CMe{\cdot}CO_2Et,$$

as sole product, and therefore differs slightly from ethyl β-imino-α-cyano-α'-methylglutarate, which yields, at the same time, a small amount of the sodium derivative having the metal attached to the same carbon atom as the alkyl group, it was thought advisable to investigate a similar compound free from nitrogen in order still further to emphasise the truth of the above generalisation. The substance chosen for experiment was ethyl carbethoxyglutaconate (X), which, since it can retain the mobile hydrogen atom, should yield the sodium compound (XI), and therefore give the alkyl derivative (XII) on alkylation:

$$(CO_2Et)_2C{:}CH{\cdot}CH_2{\cdot}CO_2Et \longrightarrow$$

(X.)

$$(CO_2Et)_2C{:}CH{\cdot}CHNa{\cdot}CO_2Et \longrightarrow (CO_2Et)_2{\cdot}C{:}CH{\cdot}CHR{\cdot}CO_2Et$$

(XI.) (XII.)

In the event of the sodium atom passing to the presumably most negative position in the system, the sodium compound would have the formula (XIII), and would therefore yield an alkyl derivative represented by (XIV):

$$(CO_2Et)CNa{\cdot}CH{:}CH{\cdot}CO_2Et \longrightarrow (CO_2Et)_2CR{\cdot}CH{:}CH{\cdot}CO_2Et$$

(XIII.) (XIV.)

The identity of the product could then be determined by hydrolysing the ester to the tricarboxylic acid, which would have either the structure (XV) or (XVI), depending on the position of the sodium atom in the original sodium derivative:

$$(CO_2H)_2C{:}CH{\cdot}CHR{\cdot}CO_2H \qquad (CO_2H)_2CR{\cdot}CH{:}CH{\cdot}CO_2H$$

(XV.) (XVI.)

As a matter of fact it was not found possible to prepare the tribasic unsaturated acid of this formula, because both acid and alkaline hydrolysis led to the formation of the alkylglutaconic acid as sole product. There is no doubt that hydrolysis by alcoholic potassium hydroxide leads to the formation of the alkali salt of the unsaturated tricarboxylic acid, but the free acid is so unstable that carbon dioxide is eliminated as soon as the alkaline solution is acidified. The difficulty was overcome by reducing the unsaturated ester to the glutaric derivative and preparing the stable, saturated tricarboxy-acid by hydrolysis with alkali. In the actual experiment, *iso*propyl iodide was used to alkylate the sodium derivative of the unsaturated ester, and the saturated tricarboxylic acid must therefore have either formula (XVII) or (XVIII), according to the original position of the sodium atom.

$$(CO_2H)_2CH{\cdot}CH{\cdot}CH(C_3H_7){\cdot}CO_2H \qquad (CO_2H)_2C(C_3H_7){\cdot}CH{\cdot}CH_2{\cdot}CO_2H.$$

(XVII.) (XVIII.)

Both these acids have been prepared, the first (XVII) by Perkin (Trans., 1896, **69**, 1492), and the second by Heinke and Perkin (*ibid.*, 1507). The former is obtained by the action of ethyl *iso*propylacrylate on ethyl sodiomalonate, and the latter by treating ethyl sodio*iso*propylmalonate with ethyl β-iodopropionate. There is therefore no doubt as to their structure, and the fact that the acid prepared by the alkylation of ethyl carbethoxyglutaconate melts at 165°, and is the same acid as that prepared by Perkin (formula XVII), is clear proof that the generalisation given at the commencement of this paper is correct.

The ethyl carbethoxyglutaconate for this experiment was prepared in the following way. Ethyl sodiomalonate was condensed with ethyl β-iodopropionate to form the well-known ethyl propane-αγγ-tricarboxylate (XIX); this was then brominated by bromine in chloroform, and the bromo-derivative (XX) boiled with diethylaniline until free from halogen.

$$(CO_2Et)_2CH\cdot CH_2\cdot CH_2\cdot CO_2Et.$$

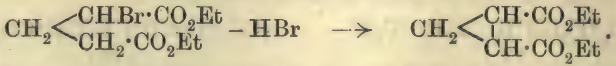
(XIX.)

$$(CO_2Et)_2CBr\cdot CH_2\cdot CH_2\cdot CO_2Et - HBr \longrightarrow$$

(XX.)

$$(CO_2Et)_2C{:}CH\cdot CH_2\cdot CO_2Et.$$

A similar reaction to this, namely, the elimination of hydrogen bromide from ethyl α-bromoglutarate (Bowtell and Perkin, *Proc.*, 1899, **15**, 241; Perkin and Tattersall, Trans., 1905, **87**, 362) has been shown to yield the *cyclo*propanedicarboxylic acid as sole product, thus:



$$CH_2{<}\begin{matrix}CHBr\cdot CO_2Et\\ CH_2\cdot CO_2Et\end{matrix} - HBr \longrightarrow CH_2{<}\begin{matrix}CH\cdot CO_2Et\\ |\\ CH\cdot CO_2Et\end{matrix}.$$

In the present experiment, the reaction led to the formation of about 80 per cent. of the unsaturated ester and 20 per cent. of the *cyclo*propane derivative, the two esters being readily separated by shaking their ethereal solution with moderately concentrated alkali, in which the glutaconic derivative dissolves as its yellow sodium derivative, $(CO_2Et)_2C{:}CH\cdot CH{:}C(ONa)\cdot OEt$.

The ester remaining in the ether gave *trans-cyclo*propane-1 : 2-dicarboxylic acid when hydrolysed.

The alkylation of ethyl β-imino-α-cyanoglutarate ceases with the introduction of two alkyl groups, and it is not possible to introduce a further alkyl group by means of sodium ethoxide and an alkyl iodide.

In a former paper (Trans., 1904, **85**, 1755) it is stated that the methylation of ethyl β-imino-α-cyano-αα′-dimethylglutarate yields the trimethyl derivative, $CO_2Et\cdot CMe(CN)\cdot C({:}NH)\cdot CMe_2\cdot CO_2Et$, but a repetition of this experiment shows that this is not the case. The trimethyl derivative, which melts at 113°, is certainly formed in small quantities by the condensation of ethyl methylcyanoacetate with its sodium derivative, and methylation of the product in situ, and it possesses the properties ascribed to it in the previous paper. The compound is, however, not identical with the product formed by the methylation of ethyl β-imino-α-cyano-αα′-dimethylglutarate, although its melting point is the same. The compound actually produced in this manner is ethyl β-imino-γ-cyano-α-methylvalerate

(XXI), and it is formed by the elimination of ethyl carbonate in accordance with the equation:

$$\begin{aligned}&\mathrm{CHMe(CN)\cdot C(:NH)\cdot CHMe\cdot CO_2Et} \text{ or}\\ &\mathrm{CO_2Et\cdot CMe(CN)\cdot C(NH_2){:}CMe\cdot CO_2Et + EtOH} \longrightarrow\\ &\qquad\underset{\text{(XXI.)}}{\mathrm{CHMe(CN)\cdot C(NH_2){:}CMe\cdot CO_2Et}} + \mathrm{CO(OEt)_2}.\end{aligned}$$

This is therefore another instance illustrating the tendency of compounds of this type to acquire the hydrogen atom necessary for tautomerism, and serves to emphasise the relationship between these imino-compounds and the simpler derivatives of ethyl glutaconate, because the above reaction is in every way analogous to that causing the formation of ethyl γ-cyano-αβγ-trimethylcrotonate and ethyl carbonate from ethyl α-cyano-αβγ-trimethylglutaconate (Trans., 1905, **87**, 1702):

$$\begin{aligned}&\mathrm{CO_2Et\cdot CMe(CN)\cdot CMe{:}CMe\cdot CO_2Et + EtOH} \longrightarrow\\ &\qquad\mathrm{CHMe(CN)\cdot CMe{:}CMe\cdot CO_2Et + CO(OEt)_2}.\end{aligned}$$

Ethyl β-imino-γ-cyano-α-methylvalerate behaves as a ketimino-enamic derivative, having a short imino-phase, and is therefore readily hydrolysed by alkalis to the ketone (XXII). The ultimate products of hydrolysis are methylmalonic and propionic acids:

$$\begin{aligned}&\mathrm{CHMe(CN)\cdot C(:NH)\cdot CHMe\cdot CO_2Et} \longrightarrow\\ &\underset{\text{(XXII.)}}{\mathrm{CHMe(CN)\cdot CO\cdot CHMe\cdot CO_2Et}} \longrightarrow \mathrm{CHMe(CO_2H)_2 + CH_3\cdot CH_2\cdot CO_2H}.\end{aligned}$$

The imino-compounds therefore fall within the generalisation given at the commencement of this paper, but with the following addition.

The imino-compounds react with sodium ethoxide in their amino-form only.

The β-imino-derivatives of the αγ-dicarboxylic esters are then derivatives of glutaconic ester, and conform, as such, to the generalisation already given.

It is unnecessary to give a large number of examples of the truth of this statement; it is sufficient to take one example of each of the three groups into which the imino-compounds have been divided (Trans., 1909, **95**, 1508).

Class I.—Imino-compounds, $\mathrm{CHX_2\cdot C(:NH)\cdot CHX_2}$ *and* $\mathrm{CHX_2\cdot C(:NH)\cdot CH_2X}$.—No substance having the first structure has as yet been prepared, although it can safely be predicted that it would not react with sodium ethoxide. The alkylation of ethyl β-imino-α-cyanoglutarate, which is a typical member of the second section, has been described in this and previous communications (*loc. cit.*).

Class II.—Imino-compounds, $\mathrm{CH_2X\cdot C(:NH)\cdot CH_2X}$ *and* $\mathrm{CH_3\cdot C(:NH)\cdot CHX_2}$.—The members of the first section react towards sodium ethoxide in the same manner as the corresponding derivative of glutaconic ester, that is to say, they react as $CH_2X{\cdot}C(NH_2){:}CHX$. With these compounds, the capacity for forming sodium derivatives is entirely determined by the tendency for the mobile hydrogen atom to pass outside the three-carbon system (compare Trans., 1911, **99**, 2188). The compounds falling within the second section are illustrated by ethyl β-imino-α-cyanobutyrate,

$$CMe({:}NH){\cdot}CH(CN){\cdot}CO_2Et$$

(Trans., 1904, **85**, 1739), and the large number of similar compounds which have been prepared. Since this substance is without a replaceable hydrogen atom in its amino-form,

$$CMe(NH_2){:}C(CN){\cdot}CO_2Et,$$

it is unacted on by sodium ethoxide.

Class III.—Imino-compounds, $CH_3{\cdot}C({:}NH){\cdot}CH_2X$.—The typical member of this group is ethyl β-iminobutyrate (ethyl β-aminocrotonate), $CH_3{\cdot}C({:}NH){:}CH_2{\cdot}CO_2Et$, which is prepared by the action of ammonia on ethyl acetoacetate. In the amino-form this compound contains one replaceable hydrogen atom; it therefore reacts with sodium ethoxide to yield a sodium derivative, from which the methyl derivative (XXIII) can be prepared by the action of methyl iodide (Conrad and Epstein, *Ber.*, 1887, **20**, 3057):

$$CH_3{\cdot}C(NH_2){:}CH{\cdot}CO_2Et \longrightarrow CH_3{\cdot}C(NH_2){:}CNa{\cdot}CO_2Et \longrightarrow$$
$$CH_3{\cdot}C(NH_2){:}CMe{\cdot}CO_2Et \text{ or } \underset{\text{(XXIII.)}}{CH_3{\cdot}C({:}NH){\cdot}CHMe{\cdot}CO_2Et}.$$

Sodium ethoxide is without further action on the methylated product.

EXPERIMENTAL.

Ethyl γ-Carbethoxyglutaconate, $(CO_2Et)_2C{:}CH{\cdot}CH_2{\cdot}CO_2Et$.

Ethyl propane-αγγ-tricarboxylate, $(CO_2Et)_2CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Et$, was prepared in the usual manner by the condensation of ethyl sodiomalonate and ethyl β-iodopropionate in alcoholic solution. The pure ester was then mixed with an equal volume of dry chloroform, two atomic proportions of dry bromine added, and the whole gently warmed on the water-bath until the colour of the bromine had practically disappeared and the evolution of hydrogen bromide had ceased. The product was then poured into water, the oil extracted by ether, and the ethereal solution, after being shaken with aqueous sodium carbonate, dried and evaporated. An analysis was made of the *ethyl γ-bromopropane-αγγ-tricarboxylate* after it had been placed in an exhausted desiccator for some days:

0·2234 gave 0·1219 AgBr. Br = 23·22.

$C_{12}H_{19}O_6Br$ requires Br = 23·6 per cent.

The figures show that the liquid consisted for the most part of the desired bromo-ester, but since it decomposed on distillation, it was not further purified, but boiled for three hours with twice its volume of freshly distilled diethylaniline. The unsaturated ester, mixed with some cyclic ester, was then isolated by pouring the cooled liquid into dilute hydrochloric acid, and extracting the oil by means of ether.

The two esters were then separated by shaking the ethereal solution with 10 per cent. aqueous potassium hydroxide until the extract ceased to be coloured yellow, when the alkaline extract was saturated with carbon dioxide and the oil which separated extracted by ether. The unsaturated ester remained as an oil on evaporating the ether, and was purified by distillation. It boiled at 183°/15 mm. as a colourless liquid:

0·1931 gave 0·3942 CO_2 and 0·1236 H_2O. C=55·67; H=7·11.

$C_{12}H_{18}O_6$ requires C=55·8; H=7·0 per cent.

The ester gives a purple colour with ferric chloride in alcoholic solution. The distillation has to be effected rapidly, since, on prolonged heating, the compound seems to undergo change, probably losing alcohol and passing into the pyrone derivative (compare Trans., 1911, **99**, 2195). The conditions of this change have not, as yet, been investigated.

The ethereal solution that remained after extracting the unsaturated ester yielded an oil on evaporation, which, since it yielded *cyclo*propane-1:2-dicarboxylic acid, melting at 173—174° (Found, C=46·01; H=4·7. Calc., C=46·1; H=4·6 per cent.), was evidently ethyl *cyclo*propane-1:1:2-tricarboxylate.

*Ethyl γ-Carbethoxy-α-*iso*propylglutaconate,*
$(CO_2Et)_2C{:}CH{\cdot}CH(C_3H_7){\cdot}CO_2Et$.

In order to prepare this ester, 2·3 grams of sodium were dissolved in 30 c.c. of alcohol, and 31 grams of ethyl carbethoxyglutaconate added to the solution; 19 grams of *iso*propyl iodide were then added, and the solution was heated on the water-bath until the deep yellow colour of the liquid has entirely disappeared, a process usually occupying three hours. The product was then poured into water, and the oil extracted in the usual manner. The ester boiled at 200—201°/16 mm. as a colourless, viscid oil:

0·1873 gave 0·4109 CO_2 and 0·1362 H_2O. C=59·83; H=8·08.

$C_{15}H_{24}O_6$ requires C=60·0; H=8·0 per cent.

The ester gives no colour with ferric chloride, and is insoluble in aqueous alkali hydroxide.

Ethyl α-isoPropylpropane-αγγ-tricarboxylate and α-isoPropylpropane-αγγ-tricarboxylic Acid.

The reduction of ethyl carbethoxyglutaconate was effected by means of sodium amalgam. Ten grams of the ester were dissolved in alcohol, and diluted with water so long as the solution remained clear. Twelve times the calculated quantity of 3 per cent. sodium amalgam was then gradually added, and a brisk current of carbon dioxide passed into the solution. When the action had ceased, the product was isolated by extraction with ether, and again treated with the same amount of sodium amalgam under similar conditions. About 5 grams of oil were extracted after the second reduction, and 15 grams of this product, collected from three experiments, were then again reduced in the same manner. The ultimate product, distilling at 208—210°/45 mm., the temperature given by Perkin (Trans., 1896, **69**, 1491), was analysed (Found, C=59·47; H=8·73. Calc., C=59·6; H=8·6 per cent.). It was hydrolysed by methyl-alcoholic potassium hydroxide in the manner described by Perkin (*loc. cit.*, p. 1492), and a tricarboxylic acid was obtained, which melted and decomposed at 165°, after recrystallisation from concentrated hydrochloric acid (Found, C=49·31; H=6·5. Calc., C=49·5; H=6·4 per cent.). The acid is evidently therefore *α-iso*-propylpropane-αγγ-tricarboxylic acid,

$$(CO_2H)_2C\cdot CH_2\cdot CH(C_3H_7)\cdot CO_2H.$$

The Action of Sodium Ethoxide on Ethyl β-Imino-α-cyano-αα′-dimethylglutarate.

Ethyl β-Imino-γ-cyano-α-methylvalerate,
$CHMe(CN)\cdot C(:NH)\cdot CHMe\cdot CO_2Et.$

This substance was originally prepared in an attempt to introduce a further methyl group into ethyl β-imino-α-cyano-αα′-dimethylglutarate. It may be prepared in almost quantitative yield in the following way. Thirteen grams of ethyl β-imino-α-cyano-αα′-dimethylglutarate, dissolved in a small quantity of alcohol, are mixed with a solution containing 1·2 grams of sodium in alcohol, and allowed to remain for one hour. At the end of this time, the dark-coloured liquid, which had an odour of ethyl carbonate, was poured into water, and the oil which separated was crystallised by scratching. The compound separates from alcohol containing a little water in colourless prisms, melting at 114—115°:

0·2154 gave 0·4669 CO_2 and 0·1489 H_2O. C=59·12; H=7·68.

$C_9H_{14}O_2N_2$ requires C=59·3; H=7·7 per cent.

The imino-compound is only slowly hydrolysed by hydrochloric acid, and has therefore a very short imino-phase.

Ethyl α'-*Cyano*-α-*propionylpropionate*, $CHMe(CN)\cdot CO\cdot CHMe\cdot CO_2Et$.

This compound is prepared from the imino-derivative by dissolving it in excess of cold aqueous potassium hydroxide, which may be effected by shaking the mixture vigorously for about five minutes, and is precipitated on the addition of hydrochloric acid. It is a liquid, boiling at 135—136°/20 mm.:

0·2073 gave 0·4469 CO_2 and 0·1351 H_2O. C = 58·79; H = 7·24.

$C_9H_{13}O_3N$ requires C = 59·0; H = 7·1 per cent.

The ester is readily soluble in aqueous potassium hydroxide, and gives a dark red colour with ferric chloride in alcoholic solution. Complete hydrolysis with alkali leads to the formation of methylmalonic and propionic acids.

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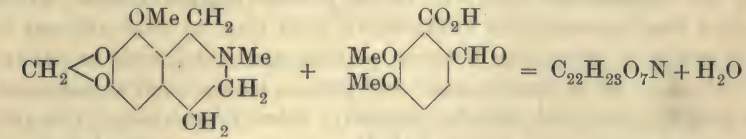
XXXII.—iso*Narcotine.*

By ERNEST GRIFFITHS JONES, WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON.

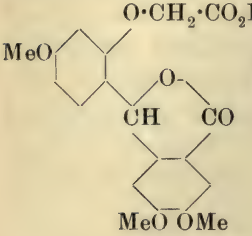
*iso*NARCOTINE was first obtained by Liebermann (*Ber.*, 1896, **29**, 184 and 2040) by the condensation of hydrocotarnine with opianic acid by means of 73 per cent. sulphuric acid:



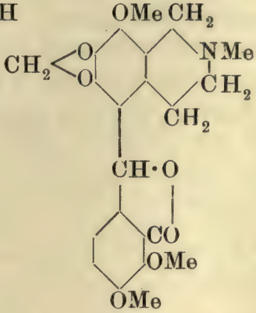
Hydrocotarnine. Opianic acid. *iso*Narcotine.

Other similar condensations were shortly afterwards investigated by Bandow (*Ber.*, 1897, **30**, 1745) and Kersten (*Ber.*, 1898, **31**, 2099), but the authors have not expressed an opinion as to the particular grouping in the hydrocotarnine molecule which takes part in the condensation with the opianic acid. Liebermann observed that *iso*narcotine is a lactone, and this behaviour, coupled with the surprising stability of the substance, as well as the fact that it yields a highly characteristic red coloration with sulphuric acid—a reaction also shown by the lactone of dihydrobrazilinic acid (I) (Trans., 1902, **81**, 1039)—led the present authors to suggest

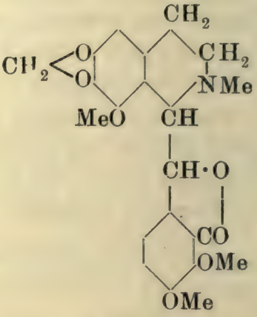
(Trans., 1911, **99**, 777) that *iso*narcotine, like the latter substance, is a meconine derivative, and probably has the constitution represented by formula (II). The nature of its isomerism with narcotine (III), which is obtained synthetically by a somewhat similar process to that employed in the synthesis of *iso*narcotine, namely, by the condensation of cotarnine with meconine (Perkin and Robinson, *loc. cit.*, p. 778), is at once evident from the comparison of the formulæ of the two substances:



(I.)



(II.)

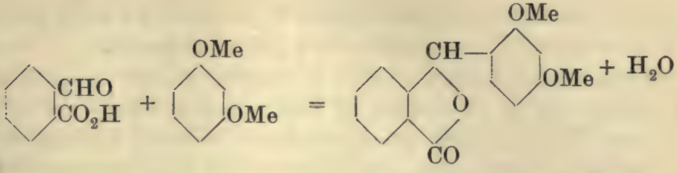


(III.)

When formula (II) was assigned to *iso*narcotine, the assumption was made that, in condensing with opianic acid in the presence of sulphuric acid, hydrocotarnine acts in its capacity as phenol ether, and this raised a slight difficulty, since Kersten (*loc. cit.*) has shown that *iso*narcotine may be produced in good yield by employing concentrated hydrochloric acid as the condensing agent, a reagent which does not appear to have been previously used in condensations with phenol ethers. This possible objection has now been removed by the experiments described in the present communication, which prove that concentrated hydrochloric acid may be most efficient in promoting condensation between *o*-aldehydic acids, such as phthalaldehydic acid or opianic acid, and phenol ethers, such as resorcinol dimethyl ether and catechol dimethyl ether (veratrole). The condensation products obtained with the aid of opianic acid dissolve in sulphuric acid with a cherry-red colour, and thus resemble *iso*narcotine. The formation of this red colour appears to be a characteristic reaction for substituted aromatic compounds which contain a free *o*- or *p*-position, and can be employed as a test for these as well as for opianic acid.

Thus, when *m*-xylene is mixed with sulphuric acid, and a trace of opianic acid added, the cherry-red colour is at once produced.

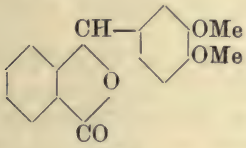
The condensations described in the present communication are, first, that between phthaldehydic acid and resorcinol dimethyl ether, when the change which occurs may be represented thus:



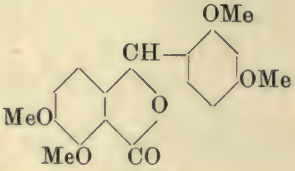
2 : 4-Dimethoxyphenylphthalide.

and that between phthaldehydic acid and catechol dimethyl ether, which results in the formation of 3: 4-dimethoxyphenylphthalide (IV).

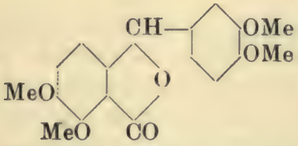
Similarly, the condensation between opianic acid and resorcinol dimethyl ether yields 2: 4-dimethoxyphenylmeconine (V), and that between opianic acid and catechol dimethyl ether gives 3:4-dimethoxyphenylmeconine (VI):



(IV.)



(V.)



(VI.)

EXPERIMENTAL.

2 : 4-*Dimethoxyphenylphthalide.*

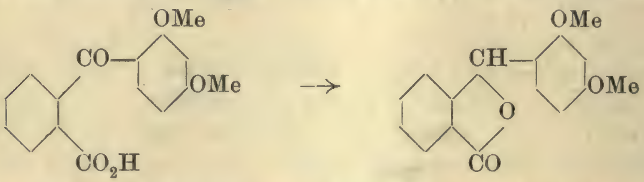
In preparing this substance, phthalaldehydic acid (5 grams) and resorcinol dimethyl ether (7 grams) were boiled with concentrated hydrochloric acid (30 c.c.) for half an hour. The mixture was distilled in a current of steam until the excess of resorcinol dimethyl ether had been removed, when, on cooling, the condensation product solidified. The mass was roughly dried and dissolved in chloroform, the extract washed with dilute sodium carbonate, and dried with anhydrous sodium sulphate.

After the removal of the solvent, the claret-coloured residue was dissolved in a little benzene, and mixed with a considerably larger amount of light petroleum (b. p. 40—60°). The filtered liquid deposited crystals, and, after recrystallisation from benzene and light petroleum, small colourless needles were obtained, which melted at 106°:

0·1610 gave 0·4215 CO_2 and 0·0762 H_2O. C = 71·4; H = 5·3.
$C_{16}H_{14}O_4$ requires C = 71·1; H = 5·3 per cent.

2:4-*Dimethoxyphenylphthalide* is readily soluble in chloroform or benzene, less so in alcohol or ether, and sparingly so in light petroleum. It is scarcely attacked when it is boiled for a short time with aqueous potassium hydroxide, but dissolves readily in alcoholic potassium hydroxide, and is not reprecipitated on the addition of water. The cautious addition of hydrochloric acid to the well-cooled solution produces a caseous precipitate, which doubtless consists of the hydroxy-acid, since it is soluble in sodium carbonate, but becomes insoluble in this reagent on warming. On recrystallisation from a mixture of benzene and light petroleum, needles of the original lactone, melting at 106°, now separate. The yellowish-red solution of the lactone in concentrated sulphuric acid becomes brownish-red on heating, and, on dilution with water, deposits a green precipitate.

In order to confirm the constitution assigned to the lactone, it was also prepared from 2′:4′-dimethoxy-2-benzoylbenzoic acid (Perkin and Robinson, Trans., 1908, **93**, 510) by reduction.



The acid, dissolved in sodium carbonate, was mechanically stirred with a large excess of 3 per cent. sodium amalgam, and, after five hours, the product was acidified with hydrochloric acid. The viscid precipitate was dissolved in chloroform, extracted with sodium carbonate, precipitated with light petroleum, and the mass extracted with a large quantity of boiling light petroleum (b. p. 50—70°). The solution, after concentration and cooling, deposited an oil, and from the clear liquid, decanted into another vessel, warty aggregates of needles gradually separated. On recrystallisation, needles melting at 106° were obtained, and that these consisted of 2:4-dimethoxyphenylphthalide was shown by the fact that the melting point remained unaltered by admixture with a specimen of this substance prepared from phthalaldehydic acid and resorcinol dimethyl ether in the manner described above.

3:4-*Dimethoxyphenylphthalide.*

The condensation of phthalaldehydic acid with catechol dimethyl ether (veratrole) was carried out exactly as described in the case of phthalaldehydic acid and resorcinol dimethyl ether. After the distillation in steam, the product remained as a cake, which soon become a brittle mass, and was more readily crystallised from solvents than the 2: 4-isomeride. 3: 4-*Dimethoxyphenylphthalide* separates from alcohol, in which it is sparingly soluble in the cold, in small, colourless, glistening plates, and melts at 148°:

0·1083 gave 0·2822 CO_2 and 0·0500 H_2O. C=71·1; H=5·1.

$C_{16}H_{14}O_4$ requires C=71·1; H=5·2 per cent.

It is readily soluble in benzene, sparingly so in alcohol, and very sparingly soluble in ether. When treated with alcoholic potassium hydroxide, it exhibits the behaviour of a lactone.

2:4-*Dimethoxyphenylmeconine and* 3:4-*Dimethoxyphenylmeconine.*

The first-mentioned of these substances was prepared from opianic acid and resorcinol dimethyl ether by the process already described, and separates from benzene in small needles, melting at 107°:

0·0781 gave 0·1878 CO_2 and 0·0393 H_2O. C=65·6; H=5·6.

$C_{18}H_{18}O_6$ requires C=65·5; H=5·5 per cent.

2: 4-*Dimethoxyphenylmeconine* is readily soluble in chloroform, benzene, hot alcohol, or acetone, very sparingly so in ether or light petroleum.

The solution in sulphuric acid is bright orange-red, and the colour is discharged on the addition of water. The behaviour of this substance with alcoholic potassium hydroxide is the same as that already described in the case of 2: 4-dimethoxyphenylphthalide.

3: 4-*Dimethoxyphenylmeconine*, produced in the same way from opianic acid and catechol dimethyl ether, separates from benzene in micro-plates, and melts at 114—115°:

0·1122 gave 0·2686 CO_2 and 0·0564 H_2O. C=65·3; H=5·6.

$C_{18}H_{18}O_6$ requires C=65·5; H=5·5 per cent.

The solution of this substance in sulphuric acid is a brilliant carmine-red, and very similar to that produced by *iso*narcotine in the same circumstances.

The authors have much pleasure in stating that the expense of this research was defrayed by grants from the Research Funds of the Royal Society and the Chemical Society.

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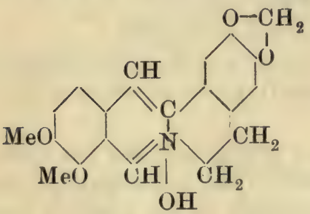
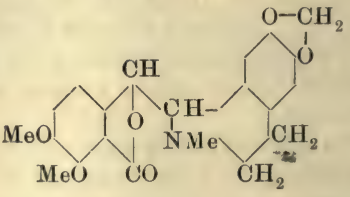
XXXIII.—iso*Oxyberberine.*

By Norman Bland, William Henry Perkin, jun., and Robert Robinson.

A short time since (Trans., 1910, **97**, 318) Perkin and Robinson reviewed the evidence on which the formula of berberine is based, and suggested that the constitution of this alkaloid is probably represented by the expression (I), which is a slight modification of the formula put forward by Perkin many years before (Trans., 1889, **55**, 1006). This view of the constitution of berberine has been accepted by Faltis (*Monatsh.*, 1910, **31**, 558), and has received support from the brilliant synthesis of berberine recently carried out by Pictet and Gams (*Ber.*, 1911, **44**, 2480).

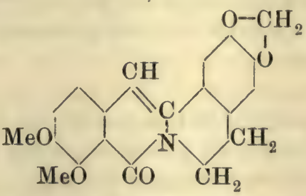


(I.)

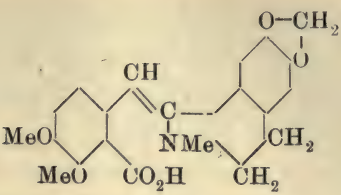


(II.)

When the formula of hydrastine (II) is written by the side of that of berberine, the relationship between these alkaloids becomes very striking, and may be expressed by the statement that hydrastine is the lactone corresponding with the unsaturated acid which would be obtained if a methyl group could be attached to the nitrogen atom of oxyberberine:

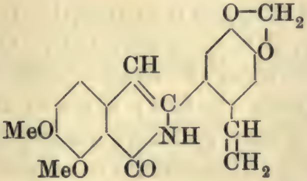


In attempting to bring about the conversion of the one alkaloid into the other, we found that oxyberberine is not acted on by methyl iodide, and we therefore investigated the action of methyl iodide in the presence of water on this substance in the hope that, under these conditions, scission of the ring and methylation might take place simultaneously. This would lead to an acid of the formula:

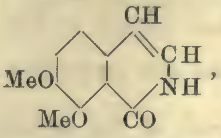


which should readily pass into hydrastine by molecular rearrangement.

No action was observed at the ordinary temperature, but on heating oxyberberine with methyl iodide and water at 150°, a new substance, melting at 245°, was obtained (oxyberberine melts at 200°), which proved to be isomeric with oxyberberine, and which we have therefore named iso*oxyberberine.* Further investigation showed that water alone does not produce this change, and there can therefore be little doubt that the function of the methyl iodide is to supply hydriodic acid, a suggestion which received support from the observation that *iso*oxyberberine is produced when oxyberberine is heated with dilute hydrochloric acid, and, indeed, this is the simplest method of preparation. *iso*Oxyberberine is less basic than oxyberberine, and crystallises from glacial acetic acid without combination with the solvent, a fact which indicates that the grouping ·CO·N· has remained, and that the smaller basicity is probably due to the removal of the alkyl-like group, $\cdot CH_2\cdot CH_2\cdot$, from the nitrogen. For these and other reasons we have suggested (Proc., 1911, **27**, 65) that iso*oxyberberine* is probably represented by the expression:



and this formula is supported by the fact that this substance readily yields an *acetyl* and a *nitroso*-derivative, and combines directly with two atoms of bromine. In some of its reactions, *iso*oxyberberine behaves as though it possessed the lactim constitution, containing the grouping ·C(OH):N·, but analogy of most of its properties to those of carbostyril, α-pyridone, and isatin seems to us to indicate that the lactam formula is the more probable. The constitution of the acetyl derivative has, however, not been demonstrated, and it is quite possible that it may contain the grouping ·C(OAc):N·. The nitroso-derivative is characterised by great stability, and is not decomposed by boiling dilute acids or alkalis, so that scission of the lactam ring has not been possible by this means, or, indeed, by any other method which we have employed. In order more clearly to understand the properties of *iso*oxyberberine, we have lately synthesised and investigated the analogously constituted dimethoxy*iso*carbostyril of the formula:



,

and hope shortly to communicate a description of this interesting substance to the Society.

EXPERIMENTAL.

Preparation and Properties of iso*Oxyberberine.*

The conversion of oxyberberine into the *iso*-compound was first effected, as has already been mentioned, by heating in sealed tubes with methyl iodide and water, but the process ultimately adopted in preparing the *iso*oxyberberine required for these experiments is the following. Oxyberberine (2 grams) is heated at 130° for five hours with water (14 c.c.) and concentrated hydrochloric acid (4 c.c.), during which the yellow colour changes to grey, but there is very little decomposition. The solid is collected and crystallised from glacial acetic acid, when pale yellow micro-needles are obtained, which melt at 245°. For analysis, the substance was dried at 100° until constant:

0·1283 gave 0·3218 CO_2 and 0·0540 H_2O. C=68·5; H=4·6.
0·1500 „ 0·3754 CO_2 „ 0·0661 H_2O. C=68·2; H=4·9.
0·1659 „ 6·3 c.c. N_2 at 19° and 760 mm. N=4·3.
$C_{20}H_{17}O_5N$ requires C=68·4; H=4·8; N=4·0 per cent.

iso*Oxyberberine* is very sparingly soluble in most solvents, and exhibits the following characteristic reactions. When an alcoholic suspension of the substance is mixed with ferric chloride, a violet coloration is produced, and, when warmed with concentrated hydrochloric acid and ferric chloride, greenish-black crystals are obtained, which dissolve in water, with separation of *iso*oxyberberine and formation of a violet solution. *iso*Oxyberberine is insoluble in aqueous or alcoholic alkali even on boiling, but, if the cold alcoholic suspension is treated with potassium hydroxide and benzenediazonium chloride, a brick-red dye is produced, and separates in flocks.

This azo-derivative dissolves in sulphuric acid to a very intensely coloured bright green solution. With other diazonium compounds, a similar behaviour is noticed; thus, diazotised naphthionic acid yields a mauve dye. *iso*Oxyberberine dissolves in sulphuric acid to a yellow solution, which becomes brownish-red on the addition of a trace of nitric acid, and, on dilution with water, a red solution is obtained. When the suspension in acetic acid is treated with sulphuric acid, the substance dissolves to a yellow solution having a bluish-green fluorescence.

*Acetyl*iso*oxyberberine.*—This derivative is readily prepared by boiling *iso*oxyberberine (2 grams) with anhydrous sodium acetate (2 grams) and acetic anhydride (5 c.c.) until a clear solution is obtained. After decomposing the excess of acetic anhydride with water, the bright yellow substance is collected, dried, and crystallised from acetic acid containing anhydride:

0·0975 gave 0·2382 CO_2 and 0·0444 H_2O. C=66·8; H=5·0.
0·1017 „ 0·2476 CO_2 „ 0·0376 H_2O. C=66·3; H=4·1.
0·2012 „ 7·2 c.c. N_2 at 22° and 756 mm. N=3·9.
$C_{22}H_{19}O_6N$ requires C=67·0; H=4·8; N=3·6 per cent.

*Acetyl*iso*oxyberberine* crystallises in hexagonal plates, and melts at 262°. When a few drops of sulphuric acid are added to the solution in acetic acid, the green fluorescence is brighter than that produced from *iso*oxyberberine under similar conditions. On boiling the solution, the acetate is hydrolysed, and *iso*oxyberberine separates, together with another substance which is soluble in alkali, but was not obtained in condition pure enough for analysis.

*Nitroso*iso*oxyberberine.*—This interesting derivative is readily prepared by shaking *iso*oxyberberine (3 grams) with *iso*amyl nitrite (12 c.c.) and acetic acid (20 c.c.) during five hours. The suspended substance is collected and crystallised from pyridine, from which it separates in intense brownish-violet, prismatic needles, melting at 263—265°:

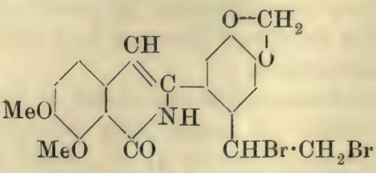
0·1362 gave 0·3122 CO_2 and 0·0512 H_2O. C=62·6; H=4·2.
0·1419 „ 0·3299 CO_2 „ 0·0562 H_2O. C=63·4; H=4·4.
0·1549 „ 9·5 c.c. N_2 at 24° and 764 mm. N=6·9.
$C_{20}H_{16}O_6N_2$ requires C=63·1; H=4·2; N=7·3 per cent.

This nitroso-derivative is remarkably stable, and is not decomposed by boiling for a considerable time with alcoholic hydrochloric acid or alcoholic potassium hydroxide. It is reduced by zinc and acetic acid to a pale yellow compound, which gives an intense purple precipitate and coloration on the addition of sodium nitrite.

*Acetyl*iso*oxyberberine Dibromide.*

The addition of bromine to *iso*oxyberberine was carried out by dissolving the substance in quantities of 1 gram in chloroform, cooling to 0°, and then adding bromine (1 mol.) dissolved in chloroform, and, after the absorption was complete, the solvent was removed by distillation.

The pale yellow crystals of iso*oxyberberine dibromide*,



which remained melted at about 242—244°. This (0·5 gram) was acetylated by boiling with sodium acetate (0·5 gram) and acetic anhydride (20 c.c.) until all had passed into solution, and then decomposing with water. The pale yellow substance which separated was crystallised from chloroform, and thus obtained in pale yellow, prismatic crystals, which melted at 230—232°:

0·1462 gave 0·0986 AgBr. Br = 28·7.

$C_{22}H_{19}O_6NBr_2$ requires Br = 29·0 per cent.

The same substance was obtained by the bromination of acetyl*iso*oxyberberine in chloroform solution.

The authors wish to state that the expense of this research was largely met by grants from the Research Funds of the Royal Society and Chemical Society.

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XXXIV.—*The Relation between the Absorption Spectra of Metallic Ions and their Valency.*

By CECIL REGINALD CRYMBLE (1851 Exhibition Research Scholar).

ALTHOUGH many observers have studied the absorption of light by solutions of inorganic compounds, no systematic attempt has been made as yet to connect the absorption spectra of such compounds with their chemical and physical properties. The selective absorption of the solutions of certain metals, such as cobalt, has been the subject of extensive investigation, whereas comparatively little attention has been paid to general absorption.

Hartley's work on the metallic nitrates (Trans., 1902, **81**, 556; 1903, **83**, 221) has shown that increase of atomic weight of the metal causes increase in general absorption, just as in the case of organic substances where increase in molecular weight is accompanied by increase in absorption. This was explained as due to the greater weight of the molecule slowing the oscillatory motion and causing absorption of rays of greater wave-length.

Drossbach (*Ber.*, 1902, **35**, 91) also maintained that solutions of the heavy metals strongly absorbed the ultra-violet rays. That atomic weight is only a factor of slight importance in causing light absorption by solutions of metals is seen when thorium is contrasted with iron. Thorium (at. wt. = 232) is about four times as heavy as iron, and is non-absorptive, whilst iron (at. wt. = 56) is markedly absorptive.

The present investigation has been confined to the absorption of light by metals in aqueous solution, and it has been found that a relation exists between the absorption of light and the valency of the metal. The absorption spectra of the salts examined may be divided into two classes: *absorptive* and *non-absorptive*. By *non-absorptive* is meant a normal solution, 10 mm. of which transmits all rays of wave-length greater than λ 2350. Rays of wave-length 2160 are transmitted by 10 mm. water, and it will be seen that solutions of most of the *non-absorptive* metals are equally transparent. Since the distinction between the two classes is not sharply marked, the wave-length 2350 has been selected as dividing the metals into two groups in accordance with their chemical properties.

The metals which yield *non-absorptive* salts are:

Li, Na, K, Rb, Cs, Gl, Mg, Ca, Ba, Sr, Zn, Cd, Th, Al, Zr.

The metals, solutions of the salts of which are *absorptive*, fall into two classes, according as they give visibly-coloured solutions, such as:

Cu, Au, Ti, Ce, V, Cr, Ur, Mn, Fe, Co, Ni, Pd, Pt,

or give colourless solutions that absorb the ultra-violet rays:

Ag, Hg, Tl, Sn, Pb, Sb, Bi.

If the chemical properties of these metals are considered, it will be seen that the metals of the *non-absorptive* group are characterised by constant valency, whilst those of the *absorptive* group are of varying valency. A metal is here regarded as of constant valency when it yields only one series of salts, the valency being determined, not by the oxides of the metals, but by its fluorides or chlorides. Oxides have been used as the means of deciding the valency of metals, but the objection, that in the case of the higher oxides the oxide may be either an "ozonide," in which the oxygen is doubly linked to the metal, or an "antozonide," in which the oxygen atoms are partly joined to one another, is only in part met by the chemical means at our disposal for distinguishing between these two types of oxides. For that reason the existence of a second series of salts has been accepted as evidence of variation in valency.

The relations between valency and absorption are rendered evident when the metals are compared according to their arrangement in the periodic classification.

After each salt is placed the wave-length up to which 10 mm. of an *N*-solution, or an equivalent length of a more dilute solution, transmit the rays of the iron arc.

Group I.

LiCl	transmits to	λ 2160	NH_4Cl	transmits to	λ 2160
NaCl	,, ,,	λ 2170	$CuSO_4$	,, ,,	λ 3150
KCl	,, ,,	λ 2160	AgF	,, ,,	λ 2560
RbCl	,, ,,	λ 2160	$AuCl_3$	,, ,,	λ 5250
CsCl	,, ,,	λ 2210			

The alkali metals yield only one fluoride, MF, and are typical of constant valency. They are quite transparent.

Copper and gold both yield two well-defined series of salts corresponding with Cu_2Cl_2,$CuCl_2$ and AuCl,$AuCl_3$. They both show strong absorption. In addition to the ordinary salts of silver, similar to AgCl, the compounds Ag_2F, Ag_2Cl, Ag_2Br, and Ag_4O are described (Abegg's "Handbuch der Anorganische Chemie," Vol. II., 1, 1908), in which silver forms a series of salts of general formula Ag_2X. The absorption of silver salts is in agreement with this.

Group II.

$GlSO_4$	transmits to	λ 2190	$BaCl_2$	transmits to	λ 2170
$MgSO_4$	,, ,,	λ 2170	$ZnSO_4$	,, ,,	λ 2170
$CaCl_2$	,, ,,	λ 2170	$CdSO_4$	,, ,,	λ 2230
$SrCl_2$	,, ,,	λ 2160	$HgCl_2$	,, ,,	λ 2660

Glucinum, magnesium, and the members of the A sub-group give one series of salts, corresponding with MCl_2. Zinc and cadmium are also of constant valency. These elements are all non-absorptive.

Mercury differs from the other members of this group, as it forms two well-defined series of salts. Its solution shows a considerable amount of absorption.

Group III.

$Al_2(SO_4)_3,(NH_4)_2SO_4$	transmits to	λ 2280	$TlCl_3$	transmits to	λ 3400
$AlCl_3$	,, ,,	λ 2350 (but lines weakened from λ 2500)			

Aluminium and thallium are the only members of this group that have been examined as yet. Aluminium is a metal of constant valency, whereas thallium forms both thallous (TlCl) and thallic ($TlCl_3$) compounds, a distinction which is reflected in their absorption spectra.

The difference in absorption between the simple and the double salt of aluminium may be due to a certain degree of residual affinity in ordinary compounds of aluminium which is completely saturated in the double salt.

Group IV.

$ZrOCl_2$ transmits to λ 2330	$SnCl_4$ …… transmits to λ 2740
$Ce(SO_4)_2$,, ,, λ 5400	$Pb(C_2H_3O_2)_2$,, ,, λ 2850
$Th(SO_4)_2$,, ,, λ 2280	

In the A sub-group titanium and cerium both give tervalent compounds, MCl_3, in addition to the quadrivalent compound, MCl_4, typical of the group. A solution of titanous chloride is deep violet, whilst solutions of ceric salts are also coloured.

Zirconium, which is intermediate between titanium and cerium, and thorium are of constant valency and are non-absorptive.

Tin and lead both give chlorides corresponding with MCl_2 and MCl_4, and both absorb light.

Group V.

$AsCl_3$ transmits to λ 2710	$BiCl_3$ transmits to λ 3700
$SbCl_3$,, ,, λ 3750	

Vanadium forms the chlorides VCl_2 and VCl_3, and its solutions are strongly coloured.

Arsenic and antimony both absorb the ultra-violet rays, and they yield the compounds $AsCl_3$,AsF_5 and $SbCl_3$,$SbCl_5$.

Bismuth forms the chlorides $BiCl_2$ and $BiCl_3$, and not only are its solutions absorbent, but the solution examined showed a deep band in the ultra-violet in Bi/1000 solution.

Group VI.—As the maximum valency allowed by the periodic law increases, the tendency towards variation in valency also increases. Chromium yields the fluorides CrF_2 and CrF_3, and uranium possesses three chlorides, UCl_3, UCl_4, UCl_5. Both these metals absorb light strongly in solution.

Group VII.—Manganese sulphate transmits to λ 2300.

In addition to the numerous oxides of manganese, the dichloride, $MnCl_2$, and the trichloride, $MnCl_3$, are known. Solutions of manganic salts are strongly coloured. Manganous salts, although of a slight pink colour in solution, are remarkably non-absorptive in the violet- and ultra-violet regions.

Group VIII.—Ferrous sulphate transmits to λ 2800.

Iron, cobalt, palladium, and platinum give coloured solutions, and they all form more than one series of salts.

Nickel, whilst giving strongly-coloured solutions, does not form any salts analogous to the ferric salts; yet evidence of its power to vary in valency is found in the complex cyanides which it yields.

The existence of the oxide, Ni_2O_3, analogous to Fe_2O_3, also shows a change in valency, further evidence being supplied by nickel carbonyl, $Ni(CO)_4$, in which the metal is apparently octavalent.

Discussion of Results.

A consideration of the results tabulated above will show that the metals, which vary in valency, give solutions characterised by their power of absorbing ultra-violet light. It has not been possible to determine whether this property is perfectly general, but about thirty-five of the commoner metals have been examined, and they are all in harmony with the rule. Apparently the metals of the rare earths may behave exceptionally; for example, the salts of neodymium are coloured, although only one chloride, $NdCl_3$, is described. Admitting these exceptions, the great majority of the metals are in agreement with the rule, and the close relationship between valency and optical properties is manifest.

Indications of further relationships between the chemical and physical properties of metals are apparent.

If the metals are arranged in order of electro-potential, as determined by the *E.M.F.* developed between metals and solutions of their salts at a given dilution, they form a series with the more electro-positive metals at one end and the less electro-positive at the other. Decrease in electro-positiveness—>

Cs, Rb, K, Na, Mg, Al, "Mn," Zn, Cd ⋮ Tl, Fe, Co, Ni, Sn, Pb, Sb, Bi, As, Cu, Hg, Ag, Pd, Pt, Au.

If a line is drawn between cadmium and thallium it divides the metals into two groups: (*a*) those to the left, the more electro-positive metals, are the metals of constant valency, and the salts of which are non-absorptive; (*b*) those to the right, the less electro-positive metals, are the metals that vary in valency, and the salts of which absorb ultra-violet light. Manganese, a metal which changes in valency, is abnormally placed between aluminium and zinc, but it is interesting to note that, whilst manganic salts are coloured, solutions of manganous salts (for example, manganous sulphate) are remarkably diactinic.

A connexion thus exists between valency, electrode-potential, and absorption of ultra-violet light. Since Drude has shown that the last property is due to the vibration of particles of sub-atomic dimensions, the underlying cause will probably be found in the motion and arrangement of the electrons.

The absorption of light by the non-metallic elements, and the effect of oxidation on the absorption of light of both metallic and non-metallic elements, are at present being studied.

EXPERIMENTAL.

Most of the salts have been examined in normal solutions, but a few comparatively insoluble ones have been examined in more dilute solutions.

The salts employed were obtained from Kahlbaum in the majority of cases, and they were subsequently purified by repeated crystallisation. Chlorides, fluorides, and sulphates have been used almost throughout, as these acidic radicles are non-absorptive.

The aluminium chloride was obtained from the solution of ammonium alum previously employed, and was photographed in a solution containing an excess of hydrochloric acid. Thallium trichloride was prepared by forming an aqueous suspension of 2·3945 grams of thallous chloride, into which chlorine was passed until all the thallous salt was dissolved. The solution was then evaporated to remove excess of chlorine, and made up with water to 100 c.c.

Solutions of the arsenic, antimony, and bismuth salts were obtained by the addition of sufficient hydrochloric acid to give a clear solution. The solutions were photographed by means of a Hilger's quartz spectrograph, an exposure of twenty seconds of the iron arc being given.

In the case of absorptive solutions the dilution is given at which the solution becomes transparent.

Salt.	Weight. Grams in c.c.	Dilution.	Thickness of layer. Cms.	Rays transmitted to λ.
LiCl	9 in 200	1·06*N*	20	2330
		,,	2	2160
NaCl	5·850 in 100	Na/1	20	2240
		,,	1	2170
KCl	7·456 in 100	K/1	10	2260
		,,	1	2160
RbCl	6·0455 in 50	Rb/1	10	2260
		,,	1	2160
CsCl	0·8418 in 50	Cs/10	10	2210
		,,	1	2170
NH_4Cl	5·351 in 100	NH_4/1	10	2170
		,,	1	2160
$CuSO_4,5H_2O$	2·4973 in 100	Cu/10	20	3150
		,,	2	2930
		Cu/1000	1	2260
AgF	1·2688 in 100	Ag/10	18	2560
		,,	2	2460
		Ag/100	1	2330
$AuCl_3,HCl,4H_2O$	2·0605 in 50	Au/10	10	5250
		,,	1	5000
		Au/10,000	1	2330
$GlSO_4,4H_2O$	8·8620 in 50	Gl/1	10	2340
		,,	1	2190
$MgSO_4,7H_2O$	24·656 in 100	Mg/1	20	2250
		,,	1	2170
$CaCl_2,6H_2O$	70 in 100	3·25 Ca	20	2330
		,,	2	2170

Salt.	Weight. Grams in c.c.	Dilution.	Thickness of layer. Cms.	Rays transmitted to λ.
$SrCl_2,6H_2O$	26·59 in 100	Sr/1	20	2330
		,,	1	2160
$BaCl_2,2H_2O$	24·433 in 100	Ba/1	19	2340
		,,	1	2170
$ZnSO_4,7H_2O$	14·375 in 50	Zn/1	10	2260
		,,	1	2170
$CdSO_4,8/3H_2O$	12·826 in 50	Cd/1	10	2330
		,,	1	2230
$HgCl_2$	1·3546 in 50	Hg/10	10	2660
		,,	1	2530
		Hg/1000	1	2300
$Al_2(SO_4)_3,(NH_4)_2SO_4,24H_2O$	9·070 in 100	Al/5	10	2280
		,,	1	2170
$AlCl_3$	—	Al/10	10	2350 (weakened from 2500)
		,,	1	2200
$TlCl_3$	—	Tl/10	20	3400
		,,	2	3200
		Tl/10,000	1	2260
$ZrOCl_2,9H_2O$	3·3968 in 100	Zr/10	18	2340
		,,	2	2250
$Ce(SO_4)_2,4H_2O$	4·0445 in 100	Ce/10	20	5400
		,,	2	4850
		Ce/10,000	1	2180
$Th(SO_4)_2,4H_2O$	2·5 in 250	Th/50	50	2280
		,,	25	2210
$SnCl_4$	13·04 in 50	Sn/1	10	2920
		,,	1	2740
		Sn/1000	1	2330
$Pb(C_2H_3O_2)_2,3H_2O$	37·922 in 100	Pb/1	20	3000
		,,	2	2850
		Pb/1000	1	2340
$AsCl_3$	from 0·9896 As_2O_3 in 100	As/10	20	2710
		,,	2	2350
$SbOCl$	1·7166 in 100	Sb/10	20	3750
		,,	1	3520
		Sb/1000	1	2380
$BiOCl$	2·5946 in 100	Bi/10	20	3700
		,,	2	3610
		Bi/10,000	1	2280
$MnSO_4,7H_2O$	27·72 in 100	Mn/1	20	2330
		,,	1	2300
$FeSO_4,7H_2O$	2·7806 in 100	Fe/10	20	3250
		,,	2	2580
		Fe/100	1	2180

Conclusions.

(1) The metallic elements may be divided into two groups: those of constant valency, the salts of which in aqueous solution transmit the ultra-violet rays, and those of varying valency, the salts of which in aqueous solution absorb ultra-violet light.

(2) If the metals are arranged according to their electrode-

potential, the more electro-positive metals are found to be of constant valency and non-absorptive.

It is desired to express thanks to Professor Letts and Dr. A. W. Stewart for kind encouragement and advice during the course of this work.

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XXXV.—*The Preparation and Properties of Sulphonic Esters.*

By JOHN FERNS and ARTHUR LAPWORTH.

THE work described in the present paper was undertaken in the hope of being able to devise a general method for the replacement of halogens attached to carbon by alkyl or aryl groups, the methods which are at present available being applicable only in rare instances. One of the results of the inquiry has been to show clearly that this object cannot be attained by the path hitherto investigated. On the other hand, many points of general interest have appeared during the course of the work, and lead to certain generalisations which may prove suggestive of further practical and theoretical developments.

At the commencement of the present research it seemed highly probable that the esters of sulphonic acids are sharply distinguished from those of carboxylic acids in at least one important particular, namely, the stability of the union between the alkyloxy-residue and the unsaturated atom which is the nucleus of the ester group, this attachment in the former series being more or less permanent, whereas in the latter series it is the link most readily severed. If the vulnerable point in each series is indicated by the dotted line as follows:

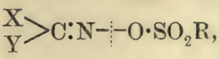
(1) $\mathrm{R{\cdot}SO_3{\cdot}O}{-}\vdots{-}\mathrm{Alk.}$ (2) $\mathrm{R{\cdot}CO}{-}\vdots{-}\mathrm{O{\cdot}Alk.}$

then most of the points in which the two series differ are summed up in simple diagrammatic manner.

It would be impossible to sum up in a short space the whole of the evidence that supports this view, and it will be sufficient at the moment to recall the fact that alkyl sulphates behave as alkylating agents towards primary, secondary, and tertiary amines, that methyl sulphate has been found to replace the ·MgX group of the Grignard reagent by the methyl group in certain cases (Werner and Zilkens, *Ber.*, 1903, **36**, 2111 and 3618; Houben, *ibid.*, 3083):

$$C_6H_5\cdot MgBr + (CH_3)_2SO_4 = C_6H_5\cdot CH_3 + CH_3\cdot SO_4\cdot MgBr.$$

Such a reaction has never been observed with carboxylic esters. Again, the characteristic mode of decomposition of the sulphonic esters of ketoximes, whereby they yield products in which the Beckmann transformation has occurred, is doubtless due to the initial resolution of the oxime ester into the parts indicated by the dotted line:



$$\begin{matrix}X\\Y\end{matrix}\!>C\colon N-\vdots-O\cdot SO_2R,$$

the condition in which the nitrogen and oxygen atoms are divorced from one another being apparently the condition provocative of this peculiar transformation of oximes. Carboxylic compounds, moreover, probably enter into reaction mainly by the formation of additive compounds at the unsaturated carboxyl group, whilst the general behaviour of sulphonic compounds suggests an entirely different mechanism of reaction.

It may be added that the observations made during the course of the work described strongly emphasise these fundamental points of difference between the two types of ester. In one reaction only, namely, that between ethyl ethanesulphonate and the Grignard reagent, was any definite evidence produced that the $\cdot SO_2\cdot$ group may display additive properties.

The examination of the behaviour of sulphonic esters towards the Grignard reagent was undertaken, in the first place, in preference to any extension of previous work with alkyl sulphates, as it appeared probable that the preparation and use of esters of the monobasic sulphonic acids would involve fewer practical complications.

Difficulties were at once encountered, however, in obtaining the sulphonic esters required for investigation, and this was found to be largely due to the fact that many sulphonic esters are highly reactive compounds, and prone to thermal and other decompositions; for example, the cause of the failure of a large number of attempts to convert benzyl alcohol directly into a sulphonic ester was traced to this property, which has still to be circumvented.

Methods of Preparation of Sulphonic Esters.

(1) Krafft and Roos (*Ber.*, 1892, **25**, 2225) prepared ethyl esters of sulphonic acids by leaving the corresponding sulphonyl chloride with excess of absolute alcohol; at the end of several days the interaction is complete, and the ester may be isolated by removing the

excess of alcohol and distillation at a low temperature in a vacuum. This method was tried by the present authors with complete success for the preparation of ethyl toluene-*p*-sulphonate, the residue obtained as above being mixed with several times its bulk of ether, shaken with dilute aqueous sodium carbonate in presence of ice, the ethereal layer separated, dried, and evaporated at the ordinary temperature. In this way a solid mass of nearly pure ester was obtained in nearly quantitative amount.

Certain dibromonaphthalenesulphonic esters are easily prepared by boiling the corresponding chlorides with excess of alcohol (Armstrong, Proc., 1891, **7**, 184). Owing, however, to the tendency towards the production of ethers and free acids, such methods are limited in applicability, and in any case only sulphonic esters of alcohols of low boiling point could readily be separated from the excess of alcohol.

(2) Another method consists in allowing the sulphonyl chloride to act on the sodium derivatives of phenols and alcohols; thus the benzene sulphonic esters of phenol, quinol, resorcinol, pyrogallol, etc., have been prepared by this method (Otto, *Ber.*, 1886, **19**, 1832, and Georgescu, *ibid.*, 1891, **24**, 416).

Methyl and ethyl benzenesulphonates were obtained by Hübner on employing alcohol-free sodium alkyloxides with ether as solvent for the sulphonyl chloride (*Annalen*, 1884, **223**, 1237). Kastle and Murrill applied a similar method in preparing *p*-iodobenzenesulphonic esters (*Amer. Chem. J.*, 1895, **17**, 292), and Miss Boyle found it satisfactory for the production of esters of di- and triiodobenzenesulphonic acids (Trans., 1910, **97**, 216 *et seq.*). The present authors have tested with great care the applicability of this method, and find that it fails in the case of benzyl alcohol and toluene-*p*-sulphonyl chloride. Even with all the precautions described by Miss Boyle, there was always obtained an oily mass from which after a time a large proportion of unchanged sulphonyl chloride separated in crystals. At the same time it was noticed that sodium toluene-*p*-sulphonate as well as chloride was formed, and that this was not due to the presence of any excess of sodium benzyloxide.

In order to determine the proportion of sulphonyl chloride which was actually decomposed by the alkyloxide, quantitative experiments were undertaken. On adding potassium benzyloxide * to an equimolecular proportion of toluene-*p*-sulphonyl chloride, both in benzene, rapid action took place; the product after remaining one night was poured into a measured volume of water, with which it was thoroughly shaken. The whole was neutral in reaction, but the amount of sodium chloride present—determined by titrating the aqueous extract—was found to represent only about 50 per cent. of that theoretically possible, so that practically one-half of the sulphonyl chloride had remained unchanged. It was therefore evident that the first product of the reaction between the alkyloxide and the sulphonyl chloride was more readily attacked by the alkyloxide than was the sulphonyl chloride itself.

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* The authors have abandoned the use of sodium in making alkyloxides for preparative work, having found that, as stated by Tschugaeff, powdered potassium is greatly to be preferred. The metal is very easily pulverised under hot benzene, and even in the cold acts on most alcohols in benzene solution with very great readiness, furnishing the potassium alkyloxides in nearly quantitative amounts and in a satisfactory condition for use.

On the other hand, no difficulty whatever was experienced in preparing the benzenesulphonic ester of menthol (first obtained in a different manner by Patterson and Frew: Trans., 1906, **89**, 332) by the foregoing method.

Sodium (2·7 grams) was powdered in the usual way below toluene, freed from toluene by successive washings with benzene, and then covered with a solution of menthol (18·7 grams) in the latter solvent. Heating for thirty-six hours on the water-bath was necessary before the sodium present had been converted into the menthyl derivative. Then benzenesulphonyl chloride (21·1 grams) was added gradually to the cooled mass, which was allowed to remain overnight. Water was next added to the mass, the whole well shaken, the benzene layer removed, washed, dried over calcium chloride, and evaporated. The residue, which became semi-solid on cooling, was pressed on a porous plate, and furnished without difficulty about 12 grams of pure menthyl benzenesulphonate, melting at 79—80°.

Bornyl toluene-p-*sulphonate*, $C_{10}H_{17}O\cdot SO_2\cdot C_7H_7$, and sulphonic esters of phenols were also found to be easily prepared by this method. A description of the former compound may be given here.

It was prepared from a well-crystallised sample of borneol, which had $[\alpha]_D^{18}+26\cdot34°$ in benzene and $[\alpha]_D^{18}+20\cdot97°$ in absolute alcohol. The ester itself was crystallised from alcohol:

0·2696 gave 0·6590 CO_2 and 0·1958 H_2O. C=66·6; H=8·1.
$C_{17}H_{24}O_3S$ requires C=66·2; H=7·8 per cent.

For the determination of its rotatory power, 1·1036 grams, made up to 50 c.c. with absolute alcohol at 20°, had α_D +0·68° in a 2-dcm. tube, whence $[\alpha]_D^{20}+15\cdot46°$.

It dissolved freely in all the usual organic media, but was insoluble in water. It crystallised from alcohol in massive prisms or tablets, which melted at 67°, and when heated further, decomposed suddenly at 132°, yielding a reddish-brown fluid, the nature of which has not yet been elucidated. The behaviour of this ester towards various agents is described elsewhere in this paper.

(3) The method of esterification due to Einhorn (*Annalen*, 1898, **301**, 95), which consists of allowing chlorides of carboxylic acids to react with alcohols in the presence of tertiary bases, is applicable in certain cases with sulphonyl chlorides, and appears to have been so employed for the first time by Patterson and Frew (Trans., 1906, **89**, 332), who prepared menthyl benzenesulphonate by this process, employing pyridine as base.

The present authors have found this method an excellent one for the preparation of bornyl *p*-toluenesulphonate and phenyl *p*-toluenesulphonate. Interaction between borneol and toluene-*p*-sulphonyl chloride in the presence of pyridine is complete in twenty-four hours at about 15°, whilst with phenol as hydroxy-compound the reaction is very rapid, and a considerable rise in temperature takes place very quickly on mixing the three components. In these cases after interaction is complete the nearly pure ester is obtained at once on pouring the mass into water. This method, however, failed completely when applied to ethyl or benzyl alcohol. When the latter was mixed with pyridine and toluene-*p*-sulphonyl chloride, a rapid change with rise in temperature took place, but in every case the products were entirely soluble in water.

This failure of methods (2) and (3) when applied to the preparation of certain sulphonic esters led the authors to investigate the nature of the changes which occur when sulphonic esters are acted on by sodium and potassium alkyloxides on the one hand, and by amines on the other.

Action of Potassium and Sodium Alkyloxides on some Sulphonyl Chlorides and Esters.

(1) Potassium benzyloxide, prepared from 3·9 grams of powdered potassium and 10·8 grams of benzyl alcohol in benzene, was added to a solution of 20 grams of ethyl toluene-*p*-sulphonate. A vigorous reaction at once took place, and a precipitate of potassium toluene-*p*-sulphonate was produced, which was collected and dried, when it was found to weigh 20 grams. The filtrate was evaporated, and warmed with alkali to decompose any unaltered sulphonic ester, the presence of which had previously been found to lead to practical difficulties. The product was poured into water, extracted with ether, dried, and the residue after evaporating off the ether was fractionated; the main bulk distilled at 98°/40 mm. This substance had all the properties of benzyl ethyl ether, the yield being about 60 per cent. of that possible. (Found, $C=79·0$; $H=8·5$. Calc., $C=79·3$; $H=8·8$ per cent.)

The main reaction between the alkyloxide and the sulphonic ester was therefore that represented by the equation:

$$C_7H_7{\cdot}SO_2{\cdot}O{\cdot}C_2H_5 + KO{\cdot}CH_2{\cdot}C_6H_5 = C_7H_7{\cdot}SO_2{\cdot}OK + C_2H_5{\cdot}O{\cdot}CH_2{\cdot}C_6H_5.$$

(2) An alcoholic solution of sodium ethoxide reacts somewhat slowly in the cold with ethyl *p*-toluenesulphonate, but the odour of ethyl ether soon becomes perceptible on warming.

(3) Sodium ($1\frac{1}{4}$ mols.) was dissolved in alcohol, and to this solution menthyl toluene-*p*-sulphonate was added. No appreciable change took place in the cold, and the whole was therefore heated on the water-bath under reflux for fourteen hours. When cooled the solution deposited crystals of sodium toluene-*p*-sulphonate, which were removed by filtration. The filtrate was distilled through a fractionating column, the residue distilled in a current of steam, and the distillate extracted with ether. In this manner menthene, to the extent of 68 per cent. of that theoretically possible, was obtained in a nearly pure state, boiling at 166—169°. (Found, C=87·7; H=13·3. Calc., C=86·9; H=13·11 per cent.)

A considerable quantity of unchanged ester was recovered from the residue from the steam-distillation. The main reaction which had occurred was evidently that represented by the equation:

$$NaO{\cdot}C_2H_5 + C_{10}H_{19}{\cdot}O{\cdot}SO_2{\cdot}C_7H_7 = NaO{\cdot}SO_2{\cdot}C_7H_7 + C_2H_5{\cdot}OH + C_{10}H_{18}.$$

(4) Bornyl toluene-*p*-sulphonate having $[\alpha]_D^{20} + 15{\cdot}46°$ in absolute alcohol was heated with sodium ethoxide during eighteen hours, and the products dealt with in much the same manner as is described in the immediately preceding section.

Some unaltered sulphonic ester was obtained as well as an oil, volatile in steam and which slowly became nearly solid when cooled in ice-water. The mass was drained on porous earthenware, and the solid portion distilled. It boiled almost constantly at 157—158°/753 mm., and subsequently melted at 52°:

1·032 grams, dissolved and made up to 50 c.c. with absolute alcohol and examined in a 2-dcm. tube, had α_D +1·60° at 20°, whence $[\alpha]_D^{20} + 38{\cdot}8°$.

The substance was identical with the camphene obtained by direct dehydration of the same specimen of borneol used in preparing the sulphonic ester (Found, C=88·1; H=11·9. Calc., C=88·2; H=11·9 per cent.), the yield of crude hydrocarbon obtained before draining being about 86 per cent. of the amount theoretically possible, allowing for the amount of ester recovered unchanged.

In this case, therefore, as in the preceding one, the main action of the alkali is to withdraw the elements of the toluenesulphonic acid from the molecule of the ester.

(5) Phenyl toluene-*p*-sulphonate (1 mol.) was added to absolute alcohol, in which sodium (1·1 mol.) had previously been dissolved. Rapid action occurred in the cold, and was completed by warming at 80°. When the products were worked up as in the two preceding sections (3 and 4), no appreciable quantity of unaltered ester was obtained, but sodium toluene-*p*-sulphonate and phenetole were isolated in nearly theoretical quantities.

In this instance, therefore, the reaction must be represented by the equation:

$$C_6H_5{\cdot}O{\cdot}SO_2{\cdot}C_7H_7 + NaO{\cdot}C_2H_5 = C_6H_5{\cdot}O{\cdot}C_2H_5 + NaO{\cdot}SO_2{\cdot}C_7H_7.$$

It may be pointed out that this must be the result of two successive changes, and for the following reason.

The reactive residues of sodium ethoxide are $Na{\cdot}$ and ${\cdot}O{\cdot}C_2H_5$. If the above change is a direct one, then the reactive residues of the ester must be $C_6H_5{\cdot}$ and ${\cdot}O{\cdot}SO_2{\cdot}C_7H_7$, and as the reaction occurs with great ease it would suggest that the attachment of the phenyl residue to oxygen in the sulphonic ester is severed in this case with extreme readiness, and those reactions which take place as the result of such a severance should occur in this case with exceptional facility; thus the ester should readily yield aniline when heated with ammonia, and diphenylamine with aniline. It was found, however, that it did not yield even traces of these substances; even at 150° phenol and sulphonic acid were the only products. In the reaction at the ordinary temperature, a fortiori, the point between the phenyl nucleus and the oxygen atom is not likely to be readily resolved. The steps in the process must therefore be:

$$\begin{aligned} C_6H_5{\cdot}O{\cdot}SO_2{\cdot}C_7H_7 + NaO{\cdot}C_2H_5 &\longrightarrow C_6H_5{\cdot}ONa + C_2H_5{\cdot}O{\cdot}SO_2{\cdot}C_7H_7 \\ &\longrightarrow C_6H_5{\cdot}O{\cdot}C_2H_5 + NaO{\cdot}SO_2{\cdot}C_7H_7. \end{aligned}$$

In support of this conclusion the authors may also state that they have observed (i) that sodium ethoxide very readily converts carboxylic esters of phenol into the sodium salt of the acid and sodium phenoxide at the ordinary temperature, and (ii) that sodium phenoxide is attacked very rapidly in the cold by ethyl toluene-*p*-sulphonate, yielding phenetole and sodium toluene-*p*-sulphonate.

Kinetic experiments are about to be undertaken with the object of testing the validity of the view here advocated.

(6) The reaction (1) in this series suggested a probable cause of the failure to obtain sulphonic esters from benzyl alcohol, and led the authors to make the following experiment:

Toluene-*p*-sulphonyl chloride (1 mol.) and potassium benzyloxide (2 mols.) suspended in benzene were mixed; after some hours the product was found to be neutral in reaction to moist litmus paper. The whole was shaken with water, and an aliquot portion of the aqueous extract titrated with silver nitrate; 96 per cent. of the total chlorine was thus found to be present as potassium chloride. The washed benzene solution was evaporated, heated with sodium hydroxide solution to remove traces of sulphonyl chloride or ester, cooled, and extracted with ether. A brown oil remained, which after repeated distillation in a vacuum gave a fraction boiling at 293—296°, consisting of benzyl ether, the amount obtained being about 48 per cent. of that theoretically possible. (Found, $C=85\cdot2$; $H=6\cdot9$. Calc., $C=84\cdot7$; $H=7\cdot1$ per cent.)

The identification was completed by heating the liquid at its boiling point, when it was gradually converted into benzaldehyde and toluene, the former being recognised with certainty.

The original reaction studied had therefore proceeded mainly in accordance with the scheme:

$$C_7H_7\cdot SO_2Cl + 2KO\cdot CH_2\cdot C_6H_5 = O(CH_2\cdot C_6H_5)_2 + KCl + C_7H_7\cdot SO_2\cdot OK.$$

Benzyl toluene-*p*-sulphonate, doubtless formed at the intermediate stage, has therefore reacted with unaltered potassium benzyloxide. The absence of appreciable quantities of ester in the previous experiments can only be explained on the supposition that the ester is nearly as reactive towards the agent as is the sulphonyl chloride.

Action of Amines on Sulphonic Esters.

The method of preparing sulphonic esters by the use of tertiary amines, used with success by Patterson and Frew in the case of menthyl benzenesulphonate, having failed in certain instances already recorded, the action of amines on certain sulphonic esters was investigated.

(1) Menthyl benzenesulphonate was scarcely affected by cold alcoholic or ethereal ammonia at temperatures above 100°, and the only evident result in any instance was hydrolysis of a trace of the ester, with formation of menthol. After treatment with dry tripropylamine even at 110°, most of the ester was recovered unchanged, and this was also the case when piperidine was used at 106°.

On the other hand, both aniline and *p*-toluidine attacked menthyl benzenesulphonate even in the cold, when in the course of time solid matter separated, whilst on warming the whole may become semi-solid. The solid matter in some experiments was removed and drained on porous earthenware, and was afterwards found to be the aniline or *p*-toluidine salt of benzenesulphonic acid. In one instance a mixture of aniline and ester was allowed to remain several days and then warmed, when it suddenly set to a semi-solid mass;

excess of alkali was added, and a current of steam passed through the liquid, the distillate extracted with ether, the latter washed with alkali, and the volatile oil which remained in the ether carefully fractionated; it was easily identified as menthene, and the amount obtained corresponded with more than 80 per cent. of that theoretically possible. The reaction had therefore proceeded mainly in accordance with the equation:

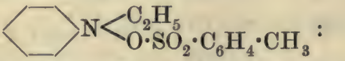
$$C_{10}H_{19}\cdot O\cdot SO_2\cdot C_6H_5 + NH_2\cdot C_6H_5 = C_{10}H_{18} + C_6H_5\cdot SO_2\cdot O\cdot NH_3\cdot C_6H_5.$$

Menthyl toluene-*p*-sulphonate behaved in a similar manner.

(2) Bornyl toluene-*p*-sulphonate ($[\alpha]_D$ + 15·46° in 2 per cent. solution in benzene) does not react with ammonia, aniline, or tripropylamine at 100°. When it is dissolved in excess of diethylaniline and the solution gradually heated, a somewhat slow reaction takes place at about 145°, accompanied by a slight darkening only. After one hour at 145—155°, the product, if acidified and distilled in a current of steam, yields more than 75 per cent. of the theoretically possible quantity of camphene, boiling at 157—158°/750 mm. The solid portion of the camphene thus obtained in one experiment, after drying on porous plates, melted at 52°, and had $[\alpha]_D^{20}$ + 38·9° in absolute alcohol.

(3) Ethyl toluene-*p*-sulphonate reacts very readily with most amines in the cold. With this ester and dry aniline in equimolecular proportions, reaction takes place almost immediately, and no detectable quantity of ethane is formed. After some hours the whole becomes semi-solid, and then consists mainly of the toluenesulphonates of aniline, ethylaniline, and diethylaniline. These three bases were separated by shaking the mixture with alkali and benzenesulphonyl chloride, removing unaltered diethylaniline in a current of steam, extracting the sulphonic derivative of monoethylaniline from the cold, strongly alkaline residue by means of ether, and then precipitating the remaining benzenesulphonanilide by addition of hydrochloride. The ethylated bases were identified without difficulty.

The action of ethyl toluene-*p*-sulphonate on pyridine, mixed in molecular proportions, also takes place in the cold, and in a few hours the whole sets to a mass of crystals. A specimen of the solid was purified by draining on porous earthenware in a vacuum, and recrystallising from a mixture of alcohol and ether. It proved to be *ethylpyridinium toluene-*p*-sulphonate*:



$$C_5H_5N{<}^{C_2H_5}_{O\cdot SO_2\cdot C_6H_4\cdot CH_3}:$$

0·2581* gave 0·5679 CO_2 and 0·1452 H_2O. C = 60·0; H = 6·2.

$C_{14}H_{17}NSO_3$ requires C = 60·2; H = 6·1 per cent.

* Dried at 130°.

It was completely soluble in water, but yielded no odour of pyridine with boiling dilute aqueous alkali. It formed *ethylpyridinium periodide* and *perbromide*, both very sparingly soluble in water. The *platinichloride* was somewhat readily soluble in water, and melted at 223—224°:

0·2200 gave 0·2206 CO_2 and 0·0710 H_2O. C = 27·3; H = 3·2.
0·1988 „ 0·0610 Pt. Pt = 30·7.
$(C_5H_5N\cdot C_2H_5)_2PtCl_6$ requires C = 27·0; H = 3·2; Pt = 31·0 per cent.

The *mercurichloride* was also prepared, and found to be somewhat readily soluble in hot water; after crystallisation from hot acetone, it formed glistening needles, which melted at 128—130°.

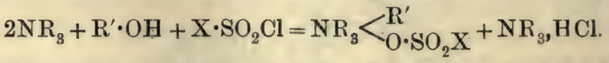
Both the platinichloride and the mercurichloride were compared directly with the corresponding compounds made from ethylpyridinium chloride, prepared by heating pyridine with ethyl chloride in a closed tube at 100°, and were found to agree in all particulars. Such a direct comparison was found necessary, as statements in a previous paper on the ethylpyridinium compounds (Meyer, *Monatsh.*, 1894, **15**, 187) were wholly at variance with the above observations. The cause of the discrepancy has not yet been traced, but the authors' object was attained by showing that the products obtained by the two different methods of alkylation were identical.

The menthyl and bornyl esters of aromatic sulphonic acids react, therefore, with tertiary amines only at somewhat elevated temperatures, yielding the same hydrocarbon as is obtained by the elimination of halogen hydride from the corresponding haloid ester.

Ethyl toluene-*p*-sulphonate, however, reacts rapidly on amines in the cold as an alkylating agent.

Direct Alkylation of Tertiary Amines by means of Alcohol and Sulphonyl Chloride.

The foregoing results indicate that the failure of Einhorn's method of esterification when applied to the production of sulphonic esters from ethyl or benzyl alcohol is due to rapid reaction of the ester first formed with the unchanged tertiary base. Experiments were therefore made with the object of achieving a direct alkylation of a tertiary base by means of a primary alcohol in presence of sulphonyl chloride, in accordance with the equation:



$$2NR_3 + R'\cdot OH + X\cdot SO_2Cl = NR_3{<}\begin{matrix}R'\\ O\cdot SO_2X\end{matrix} + NR_3,HCl.$$

Pyridine, ethyl alcohol, and toluene-*p*-sulphonyl chloride were mixed, great care being taken to avoid heating, in the quantities required by the above equation. At the end of some hours the viscid mass which resulted was shaken with water, in which it dissolved completely to a clear solution. Sodium carbonate was added, and pyridine removed by steam distillation. The residue was then concentrated, and mixed with excess of a hot saturated solution of mercuric chloride and cooled. The crystals which separated were recrystallised from acetone, and found to be identical with the ethylpyridinium mercurichloride obtained as previously described. Part of the double salt was freed from mercury by means of hydrogen sulphide, and converted into the platinichloride, which agreed in every particular with the ethylpyridinium platinichloride previously described.

In a similar experiment with a mixture of benzyl alcohol, toluene-*p*-sulphonyl chloride, and pyridine, the product obtained after several hours was completely soluble in water. It was dealt with in the manner described in the previous paragraph, and benzylpyridinium salts were isolated from it. The crystalline mercurichloride melted at 86—89°, and the platinichloride, which was very sparingly soluble in water, formed a microcrystalline powder, and when heated slowly melted at 222°. These substances were directly compared with those obtained by first benzylating pyridine with benzyl chloride, and were identical with them in all respects (see Edinger, *J. pr. Chem.*, 1890, [ii], **41**, 345).

Action of Grignard Reagent on Sulphonic Esters.

(*i*) *Ethyl Toluene*-p-*sulphonate and Magnesium Phenyl Bromide.* —Magnesium phenyl bromide, prepared from 2·4 grams of magnesium and 15·7 grams of bromobenzene in pure dry ether, was mixed with a solution of ethyl toluene-*p*-sulphonate (20 grams) in the same solvent, the whole being kept cool by means of a stream of water. A vigorous reaction at once ensued, and a white solid was deposited. At the end of about thirty-six hours water was added, and the two layers thus formed were separated.

The aqueous layer was found to contain magnesium bromide and toluenesulphonate.

The ethereal layer was washed with alkali, acid, and water successively, dried with solid potassium hydroxide, and fractionated with an efficient still-head. The following fractions were obtained: (1) boiling before 120° (mainly); (2) boiling at 125—165° (7 c.c.); (3) boiling at 165—280° (2 c.c.); (4) a residue (about 5 c.c.) of brown liquid, which solidified on cooling.

Fraction (2) was shaken repeatedly with cold 95 per cent. sulphuric acid until no further coloration of the acid was observed. The clear liquid remaining was carefully refractionated, when the main bulk passed over as a colourless liquid at 134—138°. This fraction was analysed:

0·3035 gave 1·0020 CO_2 and 0·2493 H_2O. C = 90·0; H = 9·1.

C_8H_{10} requires C = 90·6; H = 9·4 per cent.

The liquid was therefore a hydrocarbon, but contained traces of bromine. That it consisted essentially of ethylbenzene was proved by the foregoing analysis, and by the observation that on warming with chromium trioxide in acetic acid it was converted into acetophenone, easily identified by its odour and by the properties of its semicarbazone, which melted at 195—196°, whether alone or mixed with the semicarbazone from commercial acetophenone.

The remainder of fractions (2) and (3) appeared to be a mixture of benzene, ethylbenzene, and unaltered bromobenzene. Fraction (4) was almost completely volatile with steam, the distillate consisting of a white mass, which melted sharply at 70·5° and was nearly pure diphenyl.

No detectable quantity of phenylethylsulphone had been formed in the reaction; had it been present it would have occurred in fraction (4), but this was practically free from sulphur.

(ii) *Ethyl Ethanesulphonate and Magnesium Phenyl Bromide.*—Shortly after the foregoing experiment had been carried out, a paper by W. Strecker appeared (*Ber.*, 1910, **43**, 1131 *et seq.*), in which the action of magnesium phenyl bromide on ethyl ethanesulphonate (that is, *as*-diethyl sulphite) in ethereal solution was described as leading to the formation of phenylethylsulphone. As this result formed so strong a contrast with that obtained with ethyl toluenesulphonate, Strecker's experiment was repeated with 28·3 grams of ethyl ethanesulphonate, with special precautions to ensure that ethylbenzene, if formed at all, should not be overlooked.

After shaking the product of the reaction with water, the washed and dried ethereal solution was fractionated with the aid of a small but efficient column. The fraction boiling at 110—150° was treated with dilute sulphuric acid as above described, and finally yielded nearly 2 c.c. of hydrocarbon boiling at 135—141°, which was identified with ethylbenzene by converting into acetophenone.

The portion boiling above 150° was fractionated under diminished pressure, when the main bulk passed over at 160°/12 mm., solidified on cooling, and consisted of phenylethylsulphone, as stated by Strecker.

(iii) Menthyl benzenesulphonate in dry ether reacts very rapidly with magnesium ethyl bromide, a white substance being deposited. In one experiment the whole product was shaken with a little dilute hydrochloric acid and ice. The white solid which remained was separated, washed with ether, and dried; it dissolved very readily in water free from magnesium chloride, and proved to be nearly pure magnesium benzenesulphonate. The washed ethereal liquid was dried, freed from ether on the water-bath, and the residue fractionated. The main bulk passed over at 164—174°, and was easily identified as menthene.

In a parallel experiment in which magnesium *α*-naphthyl bromide was allowed to react with menthyl benzenesulphonate, similar results were obtained, but naphthalene was also isolated in considerable quantity.

(iv) Bornyl toluene-*p*-sulphonate reacted with Grignard reagents, yielding mainly hydrocarbons, including camphene. The latter is, however, accompanied by a larger quantity of hydrocarbons which remain fluid at the ordinary temperature, than when alkalis or tertiary amines act on this ester.

The reaction of the Grignard reagent with sulphonic esters may pursue one or more of three different courses, indicated by the following equations:

$$(\alpha)\ \mathrm{R{\cdot}SO_2{\cdot}OEt + XMgBr = R{\cdot}SO_2{\cdot}OMgBr + Et{\cdot}X.}$$

$$(\beta)\ \mathrm{R{\cdot}SO_2{\cdot}OEt + XMgBr = R{\cdot}SO_2X +} \left\{\begin{array}{l} \qquad \mathrm{OEt{\cdot}MgBr.} \\ ? \qquad \text{or} \\ \mathrm{C_2H_4 + HO{\cdot}MgBr.} \end{array}\right.$$

$$(\gamma)\ \mathrm{R{\cdot}SO_2{\cdot}OC_{\mathit{n}}H_{\mathit{m}+1} + XMgBr = R{\cdot}SO_2{\cdot}OMgBr + HX + C_{\mathit{n}}H_{\mathit{m}}.}$$

Conclusions.

The results so far obtained appear to show that the benzene(or *p*-toluene)-sulphonic esters of aliphatic alcohols resemble in their chemical behaviour the corresponding halide esters rather than the carboxylic esters, this being true for their reactions with alkalis and alkyloxides, with amines, and with the Grignard reagents. They are, however, much more reactive than the halide esters, in which respect as well as in some others, they recall the dialkylsulphates.

It is highly probable that the analogy between the properties of these sulphonic esters and those of the corresponding halide esters may be extended to the prediction of the general characters of a sulphonic ester when those of the halide ester are known; thus the esters of both types, when derived from the lower aliphatic alcohols, usually act as alkylating agents with, for example, amines or alkyloxides, whilst those derived from benzyl alcohol exhibit exceptionally great reactivity. Esters of borneol or menthol, on the other hand, are either almost indifferent, or, when they do suffer change, are converted mainly into the unsaturated hydrocarbon, with elimination of the elements of hydrogen halide or benzenesulphonate.

Owing to the exceptional reactivity of many sulphonic esters, no general mode of preparing them from the corresponding alcohols has yet been devised. It may be surmised, however, that (i) when the compound X·Hal is extremely stable, then the corresponding sulphonic ester, $X \cdot OSO_2 \cdot Ar$, may be prepared from the alcohol and sulphonyl chloride by means of tertiary bases, and (ii) if the reactivity of the halogen compound is of the same order as that of the ethyl or benzyl halides, then attempts to prepare the ester by this method will probably lead to alkylation of the tertiary base, whilst the action of sodium or potassium alkyloxide on the sulphonyl chloride may result in the formation of the dialkyloxide.

In case (ii) the sulphonic ester could doubtless be prepared in many instances by the action of the halide ester on the silver salt of the sulphonic acid, a method which would often fail in case (i). Probably one or other of these three methods would be applicable in all but exceptional cases.

Phenols come under the category (i), and appear to be converted into their sulphonic esters with great ease. Their sulphonic esters behave abnormally in certain respects, and are extremely stable towards amines, but highly reactive towards sodium alkyloxides, being probably converted first into sodium phenoxide and alkyl sulphonic ester, although subsequent change leads to the formation of alkyl phenyl oxide.

Another striking case of an alteration in the properties of a sulphonic ester consequent on the replacement of an aliphatic residue by an aromatic nucleus is seen on contrasting the behaviour towards magnesium phenyl bromide, of ethyl ethanesulphonate on the one hand, and ethyl toluenesulphonate on the other. In the former instance the principal product is phenylethylsulphone, only small quantities of ethylbenzene being formed; in the latter, ethylbenzene is the characteristic product, and no detectable quantity of sulphone is produced. The sulphonic group attached to the aliphatic residue thus assumes some of the characters associated with the carboxyl group, although these are absent in the aromatic sulphonic derivatives. The difference is doubtless attributable to the well known "loosening" effect of an aromatic nucleus, here exhibited in a depression of the unsaturated character of the sulphur atom to which the benzenoid nucleus is directly attached.

Experiments in extension of the observations recorded in the present communication are now in progress.

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XXXVI.—*Menthyl Nitrilotriacetate.*

By PERCY FARADAY FRANKLAND and HUGH HENRY O'SULLIVAN.

IN the course of our investigation on menthyl derivatives of substituted glycines (Trans., 1911, **99**, 2325) we endeavoured to prepare the menthyl ester of glycine itself by the action of aqueous ammonia on menthyl chloroacetate. In this we were unsuccessful, but obtained instead the menthyl ester of nitrilotriacetic acid,*

$$N(CH_2 \cdot CO_2 \cdot C_{10}H_{19})_3.$$

We have examined the rotation of this compound, both in the fused state and in methyl-alcoholic solution.

The free nitrilotriacetic acid appears to have been first obtained by W. Heintz (*Annalen*, 1862, **122**, 269) by heating monochloroacetic acid with a saturated aqueous solution of ammonia in an open vessel; the same author also described its more important properties and reactions (*Annalen*, 1865, **136**, 221). Heintz later prepared its ethyl ester by the action of ethyl iodide on the silver salt of the acid (*Annalen*, 1866, **140**, 264). A number of metallic salts are described by W. Lüddecke (*Annalen*, 1868, **147**, 272). The acid has also been prepared by Eschweiler (*Annalen*, 1894, **278**, 234) by the hydrolysis of nitrilotriacetonitrile, $N(CH_2 \cdot CN)_3$, obtained by the action of hydrogen cyanide on hexamethylenetetramine in the presence of hydrochloric acid.

As the menthyl ester melts at 80·5°, and can be readily preserved in a supercooled condition, we were able to determine the rotation over a wide range of temperature, thus:

$$[M]_D^{19^\circ} = -477 \cdot 1^\circ; \qquad [M]_D^{98^\circ} = -468 \cdot 9^\circ.$$

It is interesting to compare this rotation with that of previously known menthyl esters. This new compound is a disubstitution derivative of menthyl aminoacetate, and we (Trans., 1911, **99**, 2326) have recently shown that:

	$[M]_D^{20^\circ}$.	$[M]_D^{99^\circ}$.
Menthyl allylaminoacetate =	−160·5°	−158·8°
,, propylaminoacetate =	−158·3	−157·8

---

* The formation of this substance is of interest as showing the great stability of the menthyl esters.

and that inasmuch as these molecular rotations are almost identical with those of:

		$[M]_D^{20^\circ}$.
Menthyl propionate	=	−160·2°
,, phenylpropionate	=	−161·9
"Normal constant" of the menthyl homologous fatty esters	=	−157·8

it appears that but little change is effected in the molecular rotation by constitutional changes made in the fatty acid chain at such a remote distance from the asymmetric carbon atoms of the menthyl group. The two complex menthyl acetate groups which are attached to the nitrogen of the menthyl aminoacetate should, therefore, have no material influence on the rotation of that aminoacetate group. But the same argument may obviously be applied to each of the three similar groups respectively attached to the nitrogen, and we should anticipate, therefore, that the molecular rotation of menthyl nitrilotriacetate should be about three times that of the monomenthyl esters mentioned above. The experimental result is in surprising agreement with such anticipation, thus:

Menthyl nitrilotriacetate, $[M]_D^{19^\circ} = -477{\cdot}1^\circ \div 3 = -159{\cdot}0^\circ$

,, ,, $[M]_D^{98^\circ} = -468{\cdot}9^\circ \div 3 = -156{\cdot}3^\circ$

which are rotations, not only of the same order as, but almost identical with, those of the monomenthyl esters mentioned above.

The success of the above inference is doubtless made possible through the circumstance that the rotations of the compounds concerned have only very small temperature-coefficients; at any rate, this is the case with menthyl nitrilotriacetate and with the menthyl allylamino- and propylamino-acetates for which we have determined the rotations over a wide range of temperature; thus it will be seen from the figures cited above that one-third of the molecular rotation of menthyl nitrilotriacetate is almost identical with the molecular rotations of the menthyl allylamino- and propylamino-acetates, irrespectively of whether the comparisons are made at 20° or at about 100°.

The molecular rotations in methyl-alcoholic solution are similarly related, thus:

	$[M]_D^{20^\circ}$.
Menthyl allylaminoacetate (approximately 3 per cent. solution)	−176·8°
,, propylaminoacetate (,, ,, ,,)	−177·6
,, nitrilotriacetate (2·75 per cent. solution)	(−531·8 ÷ 3) −177·3

EXPERIMENTAL.

Thirty grams of menthyl chloroacetate were heated for twenty-eight hours at 90—100° in a sealed tube with 70 c.c. of strong aqueous ammonia (D 0·88), the latter being present to the extent of, roughly, five times the amount necessary to replace the chlorine by the amino group. On opening the tube the contents were poured out, and the gummy part washed free from ammonia with hot water. No organic substance was discoverable in the washings. The crude, insoluble gum, amounting to about 20 grams (theory, 26 grams), was crystallised from methylated spirit, and after several recrystallisations from methyl alcohol the final melting point was 80·5°. The substance separates from methyl-alcoholic solution in tufts of fine, prismatic needles, resembling thistle-down. It is insoluble in water, only soluble in methyl alcohol at 15° to the extent of about 3 per cent., but easily soluble on heating. On prolonged heating with sodium hydroxide, aqueous or alcoholic, the odour of menthol is perceived:

0·1800 gave 0·4700 CO_2 and 0·1670 H_2O. C = 71·21; H = 10·31.
0·3985 „ 8·5 c.c. N_2 (moist) at 21° and 751·5 mm. N = 2·40.
$N(CH_2{\cdot}CO_2{\cdot}C_{10}H_{19})_3$ requires C = 71·40; H = 10·41; N = 2·31 per cent.
$NH(CH_2{\cdot}CO_2{\cdot}C_{10}H_{19})_2$ requires C = 70·41; H = 10·51; N = 3·42 per cent.
$NH_2{\cdot}CH_2{\cdot}CO_2{\cdot}C_{10}H_{19}$ requires C = 67·60; H = 10·80; N = 6·57 per cent.

The substance is thus obviously menthyl nitrilotriacetate.

Densities Determined.

t	66·3°	79·8°	90·5°	99·0°
d^t_4	0·9721	0·9637	0·9559	0·9510

*Rotation in Fused State.** (Mol. wt. = 605.)

$t°$.	d^t_4.	α_D (l = 49·92 mm.).	$[\alpha]_D$.	$[M]_D$.
19·0	1·0027	−39·47°	−78·85°	−477·1°
36·2	0·9917	38·78	78·34	473·9
58·4	0·9773	38·03	77·95	471·6
79·4	0·9637	37·39	77·72	470·2
98·0	0·9515	36·81	77·50	468·9

Rotation in Methyl-alcoholic Solution.

p.	d 20°/4°.	c ($p \times d$).	$\alpha^{20°}_D$ (l = 2 dcm.).	$[\alpha]^{20°}_D$.	$[M]^{20°}_D$.
1·156	0·7944	0·9183	−1·62°	−88·22°	−533·7°
1·814	0·7951	1·443	2·54	88·03	532·6
2·749	0·7968	2·190	3·85	87·89	531·8

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* The polarimetric measurements and density determinations have been made by Mr. S. R. Carter, B.Sc.

XXXVII.—*The Constituents of Commercial Chrysarobin.*

By Frank Tutin and Hubert William Bentley Clewer.

Chrysarobin is a product obtained from Araroba or Goa powder (a deposit found in the wood of *Andira Araroba*, Aguiar) by extraction with certain solvents, such as chloroform or benzene, evaporating the extract to dryness, and powdering the residue. It has been the subject of several chemical investigations, the most important of which is that of Jowett and Potter (Trans., 1902, **81**, 1575), who fully reviewed the literature on the subject. Since the work of the above-mentioned authors a communication has appeared by Oesterle and Johann (*Arch. Pharm.*, 1910, **248**, 476), in which they showed that emodin monomethyl ether could be obtained from chrysarobin, and suggested that it was contained in the "dichrysarobin methyl ether" described by Jowett and Potter. Inasmuch as the results of no two of the previous investigations have shown any material agreement, it was deemed desirable again to examine the subject.

The results of the present investigation, which are summarised at the end of this paper, have shown that chrysarobin is a variable product, and more complicated in its nature than was heretofore supposed. Two new compounds have been isolated from it, one of which occurs in considerable proportions, and certain products previously described as individual substances have been shown to be mixtures.

Throughout the course of the work considerable difficulty has repeatedly been met with owing to the great tendency of the constituents of the chrysarobin to crystallise together, yielding products of apparent homogeneity and constancy of composition. In most cases, therefore, it was necessary, in addition to fractional crystallisation, to employ other means for the isolation of the substances described.

Experimental.

I.—*Examination of Araroba Powder.*

For the purpose of the present investigation it was thought advisable, in the first place, to make a complete examination of Araroba or Goa powder, the natural product from which chrysarobin is obtained. The material employed consisted of a good quality of the drug, which had been obtained from a trustworthy source.

As a preliminary experiment, 10 grams of the Araroba powder were extracted successively in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried at 110°, were obtained:

Petroleum (b. p. 35—50°)	extracted	3·73	grams	=	37·3	per cent.
Ether	,,	1·28	,,	=	12·8	,,
Chloroform	,,	0·27	,,	=	2·7	,,
Ethyl acetate	,,	0·14	,,	=	1·4	,,
Alcohol	,,	0·33	,,	=	3·3	,,
	Total =	5·75	grams	=	57·5	per cent.

The portion of the material left undissolved by this treatment (42·5 per cent.) consisted of dark-coloured, gummy matter and inorganic substances.

A quantity (1 kilogram) of the Araroba powder was completely extracted by continuous percolation with hot alcohol, and from the resulting extract the greater part of the alcohol was removed. The residue was then mixed with water, and distilled in a current of steam, but nothing appreciable was removed by this treatment.

The mixture remaining in the distillation flask consisted of a yellowish-brown, finely divided solid and a brown, aqueous liquid. These products were separated by filtration, and the solid washed and dried, after which it weighed 510 grams. The aqueous filtrate and washings were thoroughly examined, but they yielded only a trace of emodin monomethyl ether (m. p. 197°), some brown, amorphous material, and a small amount of a sugar which gave *d*-phenylglucosazone (m. p. 209°). No tannin was present.

The above-mentioned solid, which had been separated from the aqueous liquid, was mixed with purified sawdust, and submitted to a very thorough extraction in a large Soxhlet apparatus with petroleum (b. p. 35—50°), ether, chloroform, ethyl acetate, and alcohol.

Examination of the Petroleum Extract.

The petroleum extract of the solid consisted, for the most part, of a very sparingly soluble, orange-red powder, which amounted to 420 grams. The petroleum solution was decanted from it, and evaporated, when 2 grams of residue were obtained. This product on examination was found to consist chiefly of the anthraquinone derivatives subsequently to be described, but it also yielded a small amount of the higher fatty acids, together with a trace of a substance which appeared to be a hydrocarbon.

Isolation of Emodin, $C_{15}H_{10}O_5$.

The above-mentioned, orange-red coloured solid, which was very sparingly soluble in petroleum, was dissolved in 2 litres of chloroform, and the resulting liquid extracted successively with aqueous ammonium carbonate and sodium carbonate. During these operations appreciable quantities of a nearly black, finely divided solid separated, which gave rise to the formation of troublesome emulsions. Nothing crystalline could be obtained from the suspended solid matter, and no precipitate was formed on acidifying the filtered liquid obtained after shaking with the first-mentioned alkali. When, however, the filtered alkaline liquid obtained after shaking with aqueous sodium carbonate was acidified, a quantity (about 0·8 gram) of an orange-coloured powder separated. This was collected and recrystallised from dilute pyridine, when it formed orange-coloured needles (m. p. 252°), and was identified as emodin.* (Found, $C=66·5$; $H=3·9$. Calc., $C=66·7$; $H=3·7$ per cent.) The identity of this substance was further confirmed by its conversion into triacetylemodin, which formed slender, pale yellow prisms, melting at 194°.

Emodintridiphenylurethane, $CH_3·C_{14}H_4O_5(CO·NPh_2)_3$.—With the endeavour to form derivatives of the new compounds subsequently described, experiments were conducted with the employment of diphenylcarbamyl chloride. Although these experiments proved unsuccessful as regards the new compounds mentioned, it was found in a preliminary experiment that emodin readily yielded a *tridiphenylurethane*, a compound which has not previously been described.

A quantity (0·5 gram) of emodin was dissolved in pyridine, and the solution heated with 1·4 grams of diphenylcarbamyl chloride according to Herzog's method (*Ber.*, 1907, **40**, 1831). The resulting tridiphenylurethane separates from a mixture of alcohol and pyridine in small, pale yellow, flattened needles melting at 193°:

0·1103 gave 0·3048 CO_2 and 0·0434 H_2O. $C=75·4$; $H=4·4$.

$C_{54}H_{37}O_8N_3$ requires $C=75·7$; $H=4·3$ per cent.

Emodintridiphenylurethane is readily soluble in chloroform, benzene, or pyridine, and moderately soluble in ethyl acetate, but it dissolves only sparingly in alcohol.

Isolation of Chrysophanol,† $C_{15}H_{10}O_4$.

The original chloroform solution, from which the emodin had been removed, as above described, was evaporated, and the residue heated with a quantity of ethyl acetate. The hot mixture was then filtered, when a quantity (25 grams) of a yellow, crystalline powder was obtained. This product was found to consist of a mixture of substances, and it was therefore sought to effect a preliminary separation by fractional extraction with aqueous potassium hydroxide. Jowett and Potter (*loc. cit.*), however, obtained from commercial chrysarobin, chrysophanolanthranol ("chrysarobin" *), which, when dissolved in aqueous alkalis, is rapidly oxidised to chrysophanol. With the object, therefore, of ascertaining whether free chrysophanol was also present in the drug, the behaviour of the pure anthranol prepared by the above-mentioned investigators towards aqueous alkali of various concentrations was examined. It was then found that chrysophanolanthranol was much less acidic than the corresponding anthraquinone derivative, being only slowly removed from its solution in chloroform by a 5 per cent. solution of potassium hydroxide, whilst it was quite unaffected by a 2 per cent. solution. Chrysophanol, on the other hand, may be extracted from its solution in chloroform by a 1·5 per cent. solution of the alkali. The above-mentioned solid, which was sparingly soluble in ethyl acetate, was therefore dissolved in chloroform, and the solution shaken with ten successive portions of aqueous potassium hydroxide (1·5 per cent.). The yellow powder which was precipitated on acidifying these alkaline extracts was heated with acetic anhydride, and the resulting acetylated product fractionally crystallised. The greater part of the material was then found to be diacetylchrysophanol (m. p. 203°). The latter was hydrolysed by heating with hydrochloric acid in aqueous acetic acid solution, when chrysophanol was obtained in deep orange-coloured leaflets melting at 191°. (Found, C = 70·8; H = 4·1. Calc., C = 70·9; H = 3·9 per cent.) It is thus evident that chrysophanol is a constituent of Araroba powder, and consequently of chrysarobin. Attfield (*Pharm. J.*, 1875, [iii], **5**, 721) stated that chrysarobin consisted chiefly of "chrysophanic acid," whilst Hesse (*Annalen*, 1899, **309**, 32) denied that the latter was present, and Jowett and Potter (*loc. cit.*) did not isolate any of it.

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* Since emodinanthranol is dissolved and oxidised when shaken with aqueous sodium carbonate, there is no proof that the emodin obtained from Araroba powder did not occur partly, or possibly wholly, as the corresponding anthranol.

† The name chrysophanic acid was originally applied to a product which is now known to have consisted of a mixture of a dihydroxymethylanthraquinone, $C_{15}H_{10}O_4$, and emodin monomethyl ether. More recently, it has been applied to the former

The chloroform solution, from which the crude chrysophanol had been removed as above described, was evaporated, when the residue was found to consist of a mixture of substances which could not

compound, which was first obtained in a state of purity by Jowett and Potter (*loc. cit.*). Since, however, the dihydroxymethylanthraquinone in question is not an acid, it is much more appropriately termed chrysophanol (compare Tschirch *Arch. Pharm.*, 1912, **250**, 27).

* Since the name chrysarobin is applied to the commercial product obtained by the extraction of Araroba powder, it is considered inadvisable also to employ it as a designation for chrysophanolanthranol, as was done by Jowett and Potter (*loc. cit.*).

readily be separated by crystallisation. With the endeavour to isolate chrysophanolanthranol from this mixture, the entire material was acetylated, and the resulting product fractionally crystallised. The only compound, however, which could be separated in a state of purity was a bright yellow-coloured substance melting at 206°, of which a small amount was isolated:

0·0916 gave 0·2226 CO_2 and 0·0372 H_2O. C = 66·3; H = 4·5.

$C_{16}H_{10}O_4(OH)\cdot CO\cdot CH_3$ requires C = 66·3; H = 4·3 per cent.

This substance is thus seen to be a *monoacetyl* derivative of emodin monomethyl ether. It is removed from its solution in chloroform by dilute aqueous potassium hydroxide, and on further acetylation yields diacetylemodin monomethyl ether (m. p. 189°).

Isolation of Emodin Monomethyl Ether.

The hot ethyl acetate filtrate from the above-described solid which yielded the chrysophanol deposited on cooling about 1 gram of a crystalline substance. The latter after repeated crystallisation from ethyl acetate yielded deep orange-coloured leaflets melting at 200°, which proved to be emodin monomethyl ether. (Found, C = 67·4; H = 4·4. Calc., C = 67·6; H = 4·2 per cent.) This monomethyl ether of emodin was identical with the compound of similar nature obtained by the present authors from *Rumex Ecklonianus* (Trans., 1910, **97**, 1) and from rhubarb (Trans., 1911, **99**, 946). Its identity was further confirmed by the preparation of its diacetyl derivative, which melted at 189°, and by its hydrolysis to emodin by means of concentrated sulphuric acid.

Isolation of a New Compound, Ararobinol, $C_{23}H_{16}O_5$.

The original ethyl acetate liquid, from which the products that yielded chrysophanol and emodin monomethyl ether had been separated as above described, was evaporated to a low bulk, and about 1 litre of ether added. This precipitated a quantity (5·5 grams) of a product which was found to consist chiefly of chrysophanol, together with a small amount of emodin monomethyl ether. The ethereal filtrate from these compounds was first examined for the presence of aloe-emodin by extraction with a 0·5 per cent. solution of aqueous potassium hydroxide, but with a negative result. It was then shaken with eight successive portions of 1·5 per cent. aqueous potassium hydroxide, which treatment removed further quantities of chrysophanol and emodin monomethyl ether. The ethereal liquid was then shaken with two successive portions of 5 per cent. aqueous potassium hydroxide, when a quantity (0·2 gram) of a product was removed, which differed in appearance from the material removed by the weaker alkali solution. This product was crystallised from a mixture of ethyl acetate and glacial acetic acid, when yellow, flattened crystals were obtained, which blackened and decomposed at about 225°, but possessed no definite melting point. A further amount (about 1 gram) of the same substance was obtained on crystallising the residue left on evaporating the ethereal liquid. It was not altered by further crystallisation, and possessed all the attributes of homogeneity:

0·1109 gave 0·3016 CO_2 and 0·0468 H_2O. C = 74·2; H = 4·7.
0·0896 „ 0·2434 CO_2 „ 0·0380 H_2O. C = 74·1; H = 4·7.
$C_{23}H_{16}O_5$ requires C = 74·2; H = 4·3 per cent.

This substance does not agree in its composition and properties with any compound previously described, and it is therefore proposed to designate it *ararobinol*, with reference to the name of the material from which it was obtained.

Ararobinol is readily soluble in glacial acetic acid, but somewhat sparingly so in the other usual solvents. It is not affected by 1·5 per cent. aqueous potassium hydroxide, but dissolves fairly readily in a 10 per cent. solution of the alkali, giving a yellow liquid which does not darken appreciably on exposure to the air. When ararobinol is treated with concentrated sulphuric acid a most striking and characteristic colour reaction is produced. If the merest trace of the substance be treated with sulphuric acid, it immediately acquires an orange colour. Then, on slightly agitating the liquid, streaks of an intense blue colour appear, intermingled with the original orange colour; the blue colour then suffuses the whole liquid, which subsequently assumes a green colour, and finally a dull grey tint.

Triacetylararobinol, $C_{23}H_{13}O_5(CO{\cdot}CH_3)_3$.—A quantity of ararobinol was heated with acetic anhydride in the presence of a trace of *d*-camphorsulphonic acid. The greater part of the anhydride was then evaporated, and the residue diluted with ether, when nearly colourless, flattened prisms separated:

0·0786 gave 0·2006 CO_2 and 0·0342 H_2O. C = 69·6; H = 4·8.
$C_{29}H_{22}O_8$ requires C = 69·9; H = 4·4 per cent.

Triacetylararobinol, like its parent substance, decomposes at about 225°, and yields the above-described colour reaction on treatment with concentrated sulphuric acid.

Dihydroararobinol, $C_{23}H_{18}O_5$.—A quantity of ararobinol was heated for some hours with hydriodic acid (D 1·7), to which some glacial acetic acid had been added, but no methyl iodide was evolved. It was evident, however, that the compound had undergone some change. The contents of the flask were diluted, and the crystalline solid collected and recrystallised from glacial acetic acid. Small, greenish-yellow, rectangular plates were then obtained, which gradually blackened and decomposed at about 180°:

0·1004 gave 0·2703 CO_2 and 0·0458 H_2O. C=73·4; H=5·1.

$C_{23}H_{18}O_5$ requires C=73·8; H=4·8 per cent.

This substance is thus seen to be *dihydroararobinol.* It is sparingly soluble in the usual organic solvents, and is practically insoluble in aqueous potassium hydroxide of any concentration. It dissolves in concentrated sulphuric acid, giving an orange colour, which slowly darkens.

Oxidation of Ararobinol.—A quantity of ararobinol and an equal weight of chromic acid were dissolved in slightly diluted acetic acid, and the mixture boiled for one hour. The liquid was then poured into water and extracted with chloroform, when chrysophanol was obtained, but not in quantitative yield. The latter melted at 191°, and its identity was confirmed by the preparation of its acetyl derivative (m. p. 203°).

Isolation of Chrysophanolanthranol, $C_{15}H_{12}O_3$.

Jowett and Potter (*loc. cit.*) obtained from the petroleum extract of commercial chrysarobin by a very tedious fractional crystallisation a small amount of chrysophanolanthranol ("chrysarobin"). They also showed that the same compound could be obtained much more readily after heating the above-mentioned petroleum extract with hydriodic acid. During the foregoing experiments no chrysophanolanthranol was isolated, but indications of its presence were obtained, particularly in the feebly acidic product which was acetylated as previously described. A special search for the anthranol in question was therefore made with the employment of a further quantity of Araroba powder. A quantity (500 grams) of Araroba powder was thoroughly extracted in a Soxhlet apparatus with light petroleum, the solvent removed from the extract, and the residue digested with a limited amount of ethyl acetate, cooled, and filtered. The yellow solid so obtained was dissolved in chloroform, deprived of emodin by means of aqueous sodium carbonate, and then extracted with eighteen successive portions of a 1·5 per cent. aqueous solution of potassium hydroxide. This treatment removed a considerable amount of a mixture of chrysophanol and emodin monomethyl ether. The chloroform solution was then shaken several times with a 2 per cent. solution of the alkali to remove the last traces of the above-mentioned anthraquinone derivatives, washed, and evaporated. The residue was then fractionally crystallised many times from glacial acetic acid, when a product was obtained in yellow leaflets, which appeared to be homogeneous:

0·1000 gave 0·2746 CO_2 and 0·0458 H_2O. C = 74·9; H = 5·1.
$C_{15}H_{12}O_3$ requires C = 75·0; H = 5·0 per cent.

This product melted at 199°, and a mixture of it with pure chrysophanolanthranol prepared by Jowett and Potter by the action of hydriodic acid on chrysarobin melted at the same temperature. It exhibited all the properties of chrysophanolanthranol as described by the above-mentioned authors, but notwithstanding this fact and the excellent result it gave on analysis, it was found to be not quite pure. This was demonstrated in the following way: A quantity of the product melting at 199° was dissolved in acetic acid, chromic acid added, and the mixture heated to boiling and then poured into water. This treatment was found to convert all chrysophanolanthranol into its parent compound, but it was not a sufficiently vigorous oxidation to attack ararobinol. On working up the product it was found to consist, for the most part, of chrysophanol, but it also yielded a small amount of ararobinol. It was thus proved that chrysophanolanthranol, as obtained by us from Araroba powder, was not quite pure, and, moreover, it was found impossible to obtain a specimen of it by crystallisation alone which was free from ararobinol.

Examination of the Ethereal Extract.

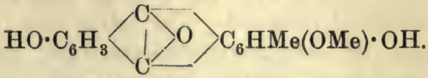
The ethereal extract of the original solid (p. 291) weighed 40 grams. It was heated with chloroform, and a small quantity of undissolved material removed. The latter was found to be the *monomethyl ether* of *dehydroemodinanthranol*, subsequently described. The chloroform solution was extracted successively with aqueous ammonium carbonate and sodium carbonate, when troublesome emulsions, caused by the separation of a fine, black powder, were formed at each operation. The solid causing these emulsions yielded nothing crystalline, as was also the case with the ammonium carbonate solution, but on acidifying the alkaline liquid obtained by extraction with sodium carbonate about 2·5 grams of emodin were obtained. The chloroform solution was then extracted with eleven successive portions of a 2 per cent. aqueous solution of potassium hydroxide, which deprived it of emodin monomethyl ether and chrysophanol, when it was washed and evaporated.

Isolation of the Monomethyl Ether of Dehydroemodinanthranol.

The yellow residue (about 8 grams) obtained on evaporating the chloroform solution as above described was digested with 800 c.c. of boiling glacial acetic acid. A quantity (0·5 gram) of material then remained undissolved, and was removed. A further amount of the same sparingly soluble compound was obtained on fractionally crystallising the material contained in the glacial acetic acid filtrate. The total amount of the compound isolated in this place was 2 grams, and it was found to be identical with the small amount of material sparingly soluble in chloroform which had been separated as above described. The compound was purified by crystallisation from a large volume of hot, glacial acetic acid, when long, pale yellow needles were obtained, which decomposed and melted at 265°:

0·0954 gave 0·2504 CO_2 and 0·0410 H_2O. C=71·6; H=4·8.
0·1013 „ 0·2660 CO_2 „ 0·0434 H_2O. C=71·6; H=4·8.
$C_{16}H_{12}O_4$ requires C=71·6; H=4·5 per cent.

This substance does not agree in its composition and properties with any compound previously described, and, as shown below, it was the anthranol of emodin monomethyl ether less 2 atoms of hydrogen. It is therefore the *monomethyl ether* of *dehydroemodinanthranol.* It was found to oxidise with markedly greater difficulty than the anthranols, and it therefore probably differs from the monomethyl ether of emodinanthranol by the loss of two atoms of hydrogen in the characteristic anthranol grouping. It may therefore be represented as follows:



$$HO\cdot C_6H_3 \langle C_2O \rangle C_6HMe(OMe)\cdot OH.$$

The monomethyl ether of dehydroemodinanthranol is very sparingly soluble, or insoluble, in the usual solvents, but is moderately soluble in warm tetrachloroethane. Its solution in organic solvents darkens somewhat on keeping, owing to the formation of an amorphous, sparingly soluble, dark-coloured decomposition product, and it is doubtless due to this property that emulsions caused by the separation of a black, amorphous powder were so frequently met with throughout the course of this work.

Action of Hydriodic Acid on the Monomethyl Ether of Dehydroemodinanthranol.—A determination of the methoxyl in the monomethyl ether of dehydroemodinanthranol was made by Perkin's modification of Zeisel's method, with the following result; it was necessary, however, to add glacial acetic acid to the hydriodic acid employed, as otherwise the methyl iodide was evolved extremely slowly:

0·2972 gave 0·2387 AgI. OMe = 10·6.
$C_{15}H_9O_3\cdot OMe$ requires OMe = 11·6 per cent.*

After the determination of the methoxyl, as above described, the flask containing the hydriodic and acetic acids was observed to contain also a quantity of a well-crystallised compound. The latter was collected, and recrystallised from a mixture of glacial acetic acid and ethyl acetate, when it formed small, yellow leaflets, which decomposed at about 255°:

0·1065 gave 0·2748 CO_2 and 0·0456 H_2O. C = 70·4; H = 4·8.
$C_{15}H_{12}O_4$ requires C = 70·3; H = 4·7 per cent.

On oxidation this substance yielded emodin (m. p. 252°), which was identified by the formation of its triacetyl derivative, and it thus appeared to be emodinanthranol. The latter compound, however, has been prepared by Krasowsky (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 1510), who described it as forming colourless crystals melting at 280°. In order, therefore, to confirm the identity of our compound (decomp. 255°) with emodinanthranol, a quantity of emodin (from rhubarb) was reduced with hydriodic acid, when a yellow-coloured anthranol was obtained. It decomposed at 255°, and was identical in all respects with the above-described compound.

Oxidation of the Monomethyl Ether of Dehydroemodinanthranol.—The monomethyl ether of dehydroemodinanthranol was not appreciably affected by a treatment with chromic acid sufficiently vigorous to convert an anthranol into the corresponding anthraquinone, but when subjected to a more energetic and prolonged treatment it underwent change.

A quantity (0·2 gram) of the dehydroanthranol, together with 0·3 gram of chromic acid, was dissolved in glacial acetic acid, and the mixture boiled for three hours. On working up the product a practically quantitative yield of emodin monomethyl ether (m. p. 200°) was obtained.

No crystalline acetyl derivative could be obtained from the monomethyl ether of dehydroemodinanthranol, and an attempt to prepare a diphenylurethane from it by heating with diphenylcarbamyl chloride in pyridine solution resulted only in the production of an intensely green liquid, from which nothing crystalline could be isolated.

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* The somewhat low result yielded by this determination is due to the great difficulty with which the methyl iodide was evolved from the compound under examination. This was proved by the fact that the crude emodinanthranol resulting from the reaction was found also to contain a small amount of emodin monomethyl ether anthranol.

The chloroform, ethyl acetate, and alcohol extracts of the original solid (p. 291) amounted to 34, 1, and 3 grams respectively. They all consisted of black, amorphous products, and nothing crystalline could be obtained from any of them.

II.—*Examination of Commercial Samples of Chrysarobin.*

Three commercial samples of chrysarobin, which may be designated as *A*, *B*, and *C* respectively, were obtained from trustworthy sources; sample *A* came from the same firm as had supplied the Araroba powder, the examination of which has just been described.

It was found that a preliminary idea of the nature of the product might be obtained by estimating quantitatively the amount of oxygen absorbed by an alkaline solution of the material. Chrysophanolanthranol, when air is passed through its solution in alkali, absorbs practically the theoretical amount of oxygen (13·3 per cent.) in about two hours. The monomethyl ether of dehydroemodinanthranol, however, is oxidised much more slowly under similar conditions, and ararobinol also appears very slowly to absorb oxygen. Known weights of the various products were therefore dissolved in a weighed amount of aqueous potassium hydroxide in a suitable apparatus, and air passed through the mixture, the necessary precautions to ensure a quantitative determination being taken. The following results were then obtained:

Material.	Weight taken.	Oxygen absorbed during first two hours.	Oxygen absorbed during fifteen hours.
Sample *A*	0·9022	6·7 per cent.	11·0 per cent.
,, *B*	0·8816	7·4 ,,	10·7 ,,
,, *C*	0·9596	5·1 ,,	10·1 ,,
Petroleum extract of Araroba powder.........	1·9130	6·9 ,,	—
Chrysophanolanthranol .	0·2340	12·8 ,,	—

From these figures it would appear that none of the commercial products consisted essentially of anthranols or similar substances, as has been indicated by the work of previous investigators.

A quantity (100 grams) of each of the samples, *A*, *B*, and *C*, was then mixed with purified sawdust, and submitted to prolonged extraction in a Soxhlet apparatus with petroleum (b. p. 35—40°), ether, and chloroform, when the entire amount of the material was removed. Although the extraction with petroleum was continued for a number of weeks, no sharp separation was effected, for it was found that the same compounds were, in each case, present in both the petroleum and ether extracts, but in different proportions. The following were the amounts of extracts obtained:

Material.	Petroleum extract.	Ether extract.	Chloroform extract.*
Sample *A*	54 grams	42 grams	0·5 gram
,, *B*	45 ,,	52 ,,	0·5 ,,
,, *C*	24 ,,	74 ,,	nil

* It was found that if the ether extraction were not carried to finality, subsequent extraction with chloroform yielded a product from which pure monomethyl ether of dehydroemodinanthranol could be obtained by a single crystallisation from acetic acid.

The petroleum and ether extracts of these samples were then separately examined according to the scheme outlined below, the chloroform extracts consisting only of amorphous products. It was necessary, however, to modify the procedure somewhat, according to the nature of the different extracts, as the products varied appreciably in their composition.

The extract to be examined was dissolved in chloroform, and the resulting solution deprived of emodin by extraction with aqueous sodium carbonate. The chrysophanol and emodin monomethyl ether were then completely removed by many extractions with 1·5 per cent. aqueous potassium hydroxide. The chloroform solution was then washed and evaporated, and the residue boiled with glacial acetic acid, when a quantity of undissolved monomethyl ether of dehydroemodinanthranol was removed by filtration from the hot liquid. The material contained in the filtrate yielded on fractional crystallisation a further quantity of the last-mentioned compound, together with ararobinol and crude chrysophanolanthranol. The anthranol, however, could never be isolated in a state of purity, and a certain proportion of the material always remained as an inseparable mixture of the various compounds described. An estimate of the amount of chrysophanolanthranol present was readily obtained by extracting the crude product from its solution in chloroform by a sufficiently concentrated aqueous alkali, when oxidation also occurred. The amount of chrysophanol formed could then readily be ascertained. In carrying out this experiment, however, it was found that some emodin monomethyl ether was also formed, thus proving the presence of a small amount of the anthranol of this compound.

The approximate composition of the three commercial samples examined is indicated on p. 302.

The bearing of the results of the present examination on the work of earlier investigators should now be considered.

The original statement by Attfield (*loc. cit.*) that chrysarobin contained chrysophanic acid, identical with that obtained from rhubarb by Schlössberger and Döpping, is strictly correct, since the latter product was really a mixture of chrysophanol and emodin

Constituent.	Percentage in sample *A*.	Percentage in sample *B*.	Percentage in sample *C*.
Chrysophanol Emodin monomethyl ether } *	6·3	7·2	8·9
Crude chrysophanolanthranol	about 26·0	about 46·0	about 62·0
Anthranol of emodin monomethyl ether	small amount	small amount	small amount
Monomethyl ether of dehydroemodinanthranol	41·1	13·4	17·7
Ararobinol	4·2	4·1	nil
Emodin	trace	nil	nil
Inseparable mixture of substances and amorphous matter	about 23·0	about 30·0	about 12·0

* About 3 or 4 parts of the former to 1 of the latter.

monomethyl ether similar to that occurring in chrysarobin (compare Trans., 1911, **99**, 946). The amount of "chrysophanic acid" indicated by Attfield to be contained in chrysarobin was, however, much greater than that actually present. Jowett and Potter (*loc. cit.*), who fully considered the work of Liebermann and Seidler (*Ber.*, 1878, **11**, 1603), of Liebermann (*ibid.*, 1881, **21**, 437; *Annalen*, 1882, **212**, 41), and of Hesse (*ibid.*, 1899, **309**, 32), stated that they had isolated from commercial chrysarobin the following substances: Chrysophanolanthranol ("chrysarobin"), "dichrysarobin," "dichrysarobin methyl ether," and a substance, $C_{17}H_{14}O_4$. In the present investigation we have confirmed the statement regarding the presence of the anthranol, but could obtain none of the other three compounds. With regard to the substance $C_{17}H_{14}O_4$, we can only say that no compound of this composition could be detected by us in any of the products examined. With regard to "dichrysarobin" and its "methyl ether," however, the experience gained during the present work led us to doubt their homogeneity; for instance, during this investigation a product was obtained which appeared to possess all the attributes of homogeneity, and which agreed approximately in its composition and properties with the "dichrysarobin methyl ether" of Jowett and Potter. It was found, however, to be a mixture of chrysophanolanthranol and the monomethyl ether of dehydroemodinanthranol, for, when subjected to a carefully regulated treatment with chromic acid, the anthranol alone was oxidised, and the resulting chrysophanol was then readily separated from the monomethyl ether of dehydroemodinanthranol. (Jowett and Potter found for "dichrysarobin methyl ether," $C = 73·0$; $H = 4·9$; $CH_3 = 2·1$ per cent.; m. p. 160°. A mixture of equal parts of chrysophanolanthranol and the monomethyl ether of dehydroemodinanthranol melts at about 170°, and requires $C = 73·3$; $H = 4·8$; $CH_3 = 2·9$ per cent.)

Now, the above-described mixture, on treatment with hydriodic acid, yields a product consisting of chrysophanolanthranol and emodinanthranol, and this product has the composition and properties assigned by Jowett and Potter to "dichrysarobin," as obtained by them after treatment of commercial chrysarobin with hydriodic acid. The specimens of "dichrysarobin" and its "methyl ether" prepared by the last-mentioned investigators being available to us, they were therefore re-examined in the light of more recent knowledge. It was thus found that when a solution of "dichrysarobin" in chloroform was shaken with 1 per cent. aqueous potassium hydroxide, emodinanthranol was removed and oxidised. On acidifying the red, alkaline liquid, emodin was obtained, its identity being confirmed by the preparation of its triacetyl derivative (m. p. 194°). The chloroform solution was then found to contain chrysophanolanthranol, which was extracted by 10 per cent. aqueous potassium hydroxide, when it was oxidised to chrysophanol. Similarly, when the specimen of "dichrysarobin methyl ether" was examined by the methods described in the present investigation, it was found to consist essentially of chrysophanolanthranol and the monomethyl ether of dehydroemodinanthranol, but it also contained small amounts of chrysophanol and emodin monomethyl ether.

The recent statement by Oesterle and Johann (*Arch. Pharm.*, 1910, **248**, 476) that chrysarobin contains emodin monomethyl ether has been confirmed, although the work of these authors did not prove that this compound existed as such in the natural material.

Summary and Conclusions.

From the results of the foregoing investigation it is seen that commercial chrysarobin is subject to considerable variation in the relative proportion of its constituents, some samples being even entirely devoid of certain compounds which occur in others. In the four products examined during the present work, chrysophanol, emodin monomethyl ether, the anthranols of these compounds,* and a new substance which proved to be the *monomethyl ether* of *dehydroemodinanthranol*, $C_{16}H_{12}O_4$, were invariably present. The original Araroba powder and two of the samples of chrysarobin also contained another new compound, *ararobinol*, $C_{23}H_{16}O_5$, whilst emodin was present in appreciable amount in the Araroba powder and to a small extent in one sample of chrysarobin. The Araroba powder also contained a small amount of a sugar which yielded *d*-phenylglucosazone and traces of the higher fatty acids, together with a product which appeared to be a hydrocarbon.

The "dichrysarobin" and "dichrysarobin methyl ether" of Jowett and Potter (Trans., 1902, **81**, 1575) have been found to be mixtures of chrysophanolanthranol and emodinanthranol, and chrysophanolanthranol and the monomethyl ether of dehydroemodinanthranol respectively. The substance, $C_{17}H_{14}O_4$, obtained by Jowett and Potter (*loc. cit.*) could not be isolated from any of the products examined by the present authors.

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* No specific test for the presence of the anthranol of emodin monomethyl ether in the Araroba powder was made, but no doubt can be entertained of its presence.

In view of the variable nature of chrysarobin it is obviously fallacious to demand that it should fulfil exact requirements regarding its solubility, etc., as is done by some national pharmacopœias, notably that of the United States; moreover, the tests given by the last-mentioned work for distinguishing commercial chrysarobin from "chrysophanic acid" are of no value, for "chrysophanic acid" does not yield the reactions there attributed to it, and, furthermore, it is invariably a constituent of chrysarobin. The general characters of commercial chrysarobin, such as are described by the British Pharmacopœia, should be sufficient for the control of the purity of the product.

There is no definite knowledge as to which constituent or constituents of commercial chrysarobin its medicinal value is to be attributed. The active constituent has generally been presumed to be chrysophanolanthranol, but there appears to be a lack of evidence to support this view, especially as the artificially prepared anthranol has been stated not to exhibit the action of the natural drug. The valuable constituent may therefore be one of the new compounds described in the present communication.

The physiological action of chrysarobin is known to be very variable (compare *Pharm. J.*, 1911, [iv], **87**, 630), and this is doubtless attributable to the differences in the composition of the drug, such as are shown in the present communication to occur. It is not easy to see, however, how a more uniform product could be obtained from the chrysarobin at present found in commerce, since it is a difficult and most tedious process to ascertain even the approximate composition of a sample of the product in question. It would nevertheless appear significant that the differences observed between the three samples examined by the present authors are, to a great extent, such as would be caused by the employment of different methods for the extraction of the original Araroba powder, or, more particularly, by the varying degrees of completeness with which the extraction had been conducted. It is probable, therefore, that commercial chrysarobin would be of much more uniform composition if a definite solvent could be adopted for the extraction of the Araroba powder, and the extraction always made complete.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
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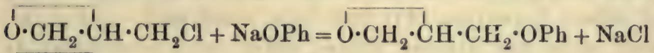
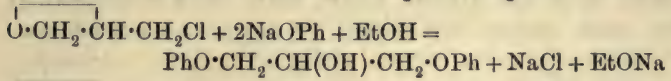
XXXVIII.—*The Aryl Ethers of Glycide, Glycerol, and Glycerol-a-monochlorohydrin.*

By ERNEST ROBERT MARLE.

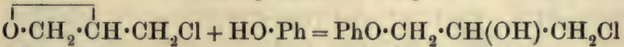
It was shown by Lindeman (*Ber.*, 1891, **24**, 2145) that epichlorohydrin may react with sodium phenoxide in two ways, giving phenyl glycide ether or glycerol diphenyl ether, according as one or both ends of the chain take part. Lindeman also obtained the phenyl ether of glycerol-α-monochlorohydrin in an impure form by heating epichlorohydrin with phenol for some hours at 150°. He showed, further, that the glycide ether reacts with water to give an aryl ether of glycerol, and with sodium phenoxide giving glycerol diphenyl ether, and that the aryl ether of glycerol-α-monochlorohydrin reacts with sodium hydroxide, giving the glycide ether. These reactions are represented by equations (1) to (6):



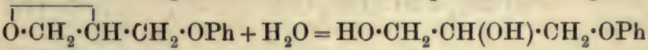
$$\overline{O\cdot CH_2\cdot CH}\cdot CH_2Cl + NaOPh = \overline{O\cdot CH_2\cdot CH}\cdot CH_2\cdot OPh + NaCl \quad . \quad . \quad (1)$$



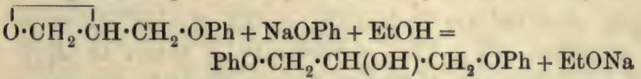
$$\overline{O\cdot CH_2\cdot CH}\cdot CH_2Cl + 2NaOPh + EtOH = PhO\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OPh + NaCl + EtONa \quad . \quad . \quad (2)$$



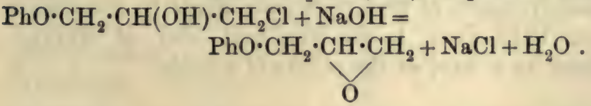
$$\overline{O\cdot CH_2\cdot CH}\cdot CH_2Cl + HO\cdot Ph = PhO\cdot CH_2\cdot CH(OH)\cdot CH_2Cl \quad . \quad . \quad . \quad (3)$$



$$\overline{O\cdot CH_2\cdot CH}\cdot CH_2\cdot OPh + H_2O = HO\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OPh \quad . \quad . \quad (4)$$



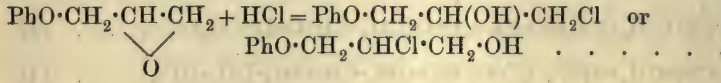
$$\overline{O\cdot CH_2\cdot CH}\cdot CH_2\cdot OPh + NaOPh + EtOH = PhO\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OPh + EtONa \quad . \quad . \quad . \quad (5)$$



$$PhO\cdot CH_2\cdot CH(OH)\cdot CH_2Cl + NaOH = PhO\cdot CH_2\cdot \underbrace{CH\cdot CH_2}_{O} + NaCl + H_2O \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Reactions (1) and (2) were afterwards employed by Boyd (Trans., 1901, **79**, 1221; 1903, **83**, 1135), who investigated the behaviour of several glycerol diaryl ethers towards the chlorides of phosphorus. Since then Cohn and Plohn (*Ber.*, 1907, **40**, 2597) and Zunino (*Atti R. Accad. Lincei*, 1909, [v], **18**, i, 254) obtained results at variance with those of Lindeman and Boyd, which, however, Boyd and Marle (Trans., 1908, **93**, 838; 1909, **95**, 1807) have shown to be incorrect, Lindeman's view of reactions (1), (2), and (5) being definitely established. More recently, Boyd and Marle (Trans., 1910, **97**, 1788) have observed that epichlorohydrin can also react with sodium phenoxide to produce the phenyl ether of glycerol-α-monochlorohydrin, and have shown how this reaction may be employed conveniently for the preparation of the aryl ethers of glycerol-α-monochlorohydrin.

In the papers referred to above, a number of glycide aryl ethers, glycerol diaryl ethers, and ethers of glycerol-*α*-monochlorohydrin have been described, and the object of the present research was primarily to complete the series of these derivatives of glycerol and the more important phenols. At the same time, the action of the *α*-monochlorohydrin on phenols in alkaline solution has been investigated, and several new glycerol monaryl ethers are described in this paper. This part of the work was undertaken, in the first place, in order to find out if these glycerol monaryl ethers might have been mistaken by Zunino or by Fourneau (*J. Pharm. Chim.*, 1910, [vii], **1**, 55 *et seq.*) for the glycide ethers or the diaryl glycerol ethers; this supposition proved to be unfounded. Some of the glycerol monaryl ethers have been prepared by Schivkovitch (*Monatsh.*, 1908, **29**, 951) by another method, and Fourneau has recently (D.R.-P. 219325) used the above method to prepare the *o*- and *p*-chlorophenyl ethers of glycerol. The observation of Lindeman that the glycide ethers react with water to produce glycerol aryl ethers [equation (4)] has been confirmed, and it is further proved that the glycide ethers react with concentrated hydrochloric acid, giving aryl ethers of glycerol-*α*-monochlorohydrin:



$$\underbrace{PhO\cdot CH_2\cdot CH\cdot CH_2}_{O} + HCl = PhO\cdot CH_2\cdot CH(OH)\cdot CH_2Cl \quad \text{or} \quad PhO\cdot CH_2\cdot CHCl\cdot CH_2\cdot OH \quad . \; . \; . \; . \; . \; . \; . \quad (7)$$

and these again with sodium hydroxide, giving glycide ethers as indicated in equation (6). The opportunity is taken to draw attention to the incorrectness of the statements made by Fourneau (*J. Pharm. Chim.*, 1910, [vii], **1**, 55, 97), and also of Zunino (*loc. cit.*) with regard to several of the ethers of glycide.

General Methods of Preparation.

When the sodium derivative of a phenol is mixed with *α*-dichlorohydrin and allowed to remain for some days at the ordinary temperature, the glycide ether, the aryl ether of glycerol-*α*-monochlorohydrin, and the diaryl ether of glycerol are formed. This method, which is described by Fourneau, was rejected after a trial, as the yield of each compound is poor, and it was found difficult to separate the products satisfactorily from one another.

When epichlorohydrin is heated with phenol, either in a sealed tube or under reflux, the phenyl ether of glycerol-*α*-monochlorohydrin is produced, along with substances of high boiling point. According to Lindeman, heating phenol with epichlorohydrin in a sealed tube gives phenyl glycide ether as well as the phenyl ether of glycerol-α-monochlorohydrin, and Fourneau (*loc. cit.*) states that he has also in this way obtained both of these products, together with glycerol diphenyl ether.

Boyd and Marle, however, could obtain no evidence of the formation of the glycide ether in these circumstances, and indeed it is difficult to understand how this substance could be formed, as no hydrogen chloride is evolved. On boiling a mixture of phenol and epichlorohydrin under reflux for twenty-four hours the author has not been able to detect the presence of any phenyl glycide ether among the products. On extracting the dark-coloured reaction mixture with ether, washing with aqueous sodium hydroxide, drying over anhydrous potassium carbonate, evaporating the ether, and distilling under diminished pressure, the boiling point was found to rise continuously from below 100° to above 270° (16 mm.). About 20 grams of impure phenyl ether of glycerol-α-monochlorohydrin were obtained from 47 grams of phenol and 45 grams of epichlorohydrin, that is, about 22 per cent.

EXPERIMENTAL.

For the preparation of the glycide ethers described below, the method adopted was that used previously by Lindeman (*loc. cit.*) and by Boyd and Marle (Trans., 1908, **93**, 838); the small quantity of the aryl ether of glycerol-α-monochlorohydrin that is produced simultaneously is easily removed by warming the crude product with solid sodium hydroxide; unless care is taken, however, the glycide ether is transformed into products of high boiling point, probably owing to a process of polymerisation. In all cases the glycide ether is readily separated from the diaryl glycerol ether by distillation.

For the preparation of the diaryl ethers of glycerol Lindeman's method (*loc. cit.*) was employed.

For the preparation of the aryl ethers of glycerol-α-monochlorohydrin the method described by Boyd and Marle (Trans., 1910, **97**, 1788) was used.

A modification of this method was necessary in some cases, and is described below.

m-*Tolyl Glycide Ether.*—This compound was prepared in the usual way. After three fractionations under diminished pressure a colourless oil was obtained, boiling at 139·5—140°/15 mm. (corr.):

0·1916 gave 0·5129 CO_2 and 0·1248 H_2O. C=73·01; H=7·29.

$C_{10}H_{12}O_2$ requires C=73·13; H=7·38 per cent.

s-*Tribromophenyl Glycide Ether,* $C_9H_7O_2Br_3$.—This substance was prepared by Cohn and Plohn (*Ber.*, 1907, **40**, 2597), but the melting point given (85°) is too low. Three grams of epichlorohydrin, 10·8 grams of tribromophenol, 2 grams of sodium hydroxide, and 100 c.c. of water were allowed to remain at the ordinary temperature for some days; the resulting oil was poured into excess of water, when a solid separated which was recrystallised from alcohol. After further recrystallisation from alcohol, hair-like, microscopic needles were obtained, melting at 109—110° (corr.). The substance is sparingly soluble in light petroleum. (Found, Br = 62·07. Calc., Br = 61·98 per cent.)

p-*Nitrophenyl Glycide Ether*.—Epichlorohydrin (23 grams), *p*-nitrophenol (34·7 grams), sodium hydroxide (12·5 grams), and water (400 c.c.) were left for some days at the ordinary temperature. A yellow solid was formed, and this was washed with dilute aqueous sodium hydroxide to remove unchanged *p*-nitrophenol. The whole was soluble in alcohol, and, on keeping, two solids appeared, the one separating at first as an oil, the other as a solid. The glycide ether is sparingly soluble in boiling water, and was separated from the mixture by boiling repeatedly with the same quantity of water, cooling, and collecting the crystals which separated. It was then recrystallised several times from alcohol. The pure substance has a faint yellow colour, which is not diminished by washing with aqueous sodium hydroxide or by recrystallisation, and melts at 67° (corr.). (Fourneau gives m. p. 69°):

0·2407 gave 0·4920 CO_2 and 0·1024 H_2O. C = 55·75; H = 4·76.
0·4545 „ 28·25 c.c. N_2 (moist) at 17° and 752 mm. N = 7·14.
$C_9H_9O_4N$ requires C = 55·37; H = 4·65; N = 7·18 per cent.

Carvacryl Glycide Ether.—This was prepared in the usual way, and after nine fractionations under diminished pressure a colourless oil was obtained, boiling at 157°/14·5 mm. (corr.):

0·2942 gave 0·8165 CO_2 and 0·2281 H_2O. C = 75·69; H = 8·68.
$C_{13}H_{18}O_2$ requires C = 75·68; H = 8·80 per cent.

Guaiacyl Glycide Ether, $C_{10}H_{12}O_3$.—The reaction between guaiacol and epichlorohydrin is energetic in the presence of sodium hydroxide, and if the mixture is left too long glycerol diguaiacyl ether is the main product. On fractionating under diminished pressure, an oil was obtained, boiling at 165°/20 mm. (corr.) (Fourneau gives 170°/16 mm., but no analyses), which crystallised readily. After being recrystallised twice from hot water and then from light petroleum, the substance melted at 36° (corr.) (Fourneau gives 79·5°):

0·2790 gave 0·6813 CO_2 and 0·1674 H_2O. C = 66·60; H = 6·71.
$C_{10}H_{12}O_3$ requires C = 66·63; H = 6·72 per cent.

a-Naphthyl Glycide Ether, $C_{13}H_{12}O_2$.—This compound is an almost colourless oil, boiling at 203—203·5°/15 mm. (corr.). Lindeman gives 263°/200 mm. (Found, C=77·99; H=5·87. Calc., C=77·96; H=6·05 per cent.)

Glycerol Di-s-tribromophenyl Ether.—Tribromophenol (13 grams), epichlorohydrin (1·8 grams), and sodium (0·5 gram) in alcohol (20 c.c.) were heated under reflux for two hours in a water-bath. After three-quarters of an hour a white, bulky solid appeared. Water was added, and the solid was collected, washed with aqueous sodium hydroxide, dried, and recrystallised from boiling benzene. It forms colourless, microscopic prisms, very soluble in boiling alcohol, and melting at 200° (corr.):

0·1735 gave 0·2726 AgBr. Br=66·86.

$C_{15}H_{10}O_3Br_6$ requires Br=66·82 per cent.

*Glycerol Di-*p*-nitrophenyl Ether*, $C_{15}H_{14}O_7N_2$.—The yellow solid which results from heating together *p*-nitrophenol, epichlorohydrin, and sodium ethoxide in alcohol is very sparingly soluble in ether. It was washed with aqueous sodium hydroxide until almost colourless, recrystallised from alcohol, then from a mixture of ethyl and methyl alcohols. (Fourneau states that the substance is more soluble in methyl alcohol than in ethyl alcohol; this is not so to an appreciable extent.) After recrystallising twice from acetone it was obtained in fine, silky needles, melting at 145° (corr.). The substance is soluble in ether, boiling ethyl and methyl alcohols, dilute ethyl alcohol, or boiling acetone. (Found, N=8·42. Calc., N=8·38 per cent.)

Glycerol Dicarvacryl Ether.—Zunino (*loc. cit.*) claimed to have prepared this substance, but as he gives 245—246° (presumably at atmospheric pressure) as the boiling point he can hardly have obtained the substance pure. On pouring the reaction mixture into water a viscid oil resulted, which was extracted with light petroleum, washed, and, after evaporation of the petroleum, distilled under diminished pressure. After four fractionations a colourless oil was obtained boiling at 268°/16·5 mm. (corr.). The oil has a very faint yellow colour, most likely due to slight decomposition on distillation. It is very viscous, but does not solidify on keeping:

0·2766 gave 0·7843 CO_2 and 0·2229 H_2O. C=77·33; H=9·02.

$C_{23}H_{32}O_3$ requires C=77·52; H=8·98 per cent.

Glycerol diguaiacyl ether is precipitated as an oil from solution in alcohol on adding water, and solidifies on standing. By recrystallisation twice from dilute alcohol, then twice from alcohol, it was obtained as a crystalline solid, melting at 72·5° (corr.):

0·2166 gave 0·5348 CO_2 and 0·1362 H_2O. C = 67·34; H = 7·04.
$C_{17}H_{20}O_5$ requires C = 67·07; H = 6·63 per cent.

Glycerol Di-a-naphthyl Ether.—Several attempts were made to obtain this compound by the usual method; a very viscous oil was obtained, which solidified very slowly on keeping.

All attempts to recrystallise it failed, as it proved to be extremely soluble in all the ordinary solvents (alcohol, ether, acetic acid, ethyl acetate, acetone, light petroleum, chloroform, benzene, or toluene), and on evaporation of the solvent was left as a viscous oil, which eventually solidified to a dark yellow, vitreous mass on removing the last traces of the solvent. Even using a Fleuss pump distillation was very slow, and was accompanied by much decomposition, the boiling point being above 300°/3 mm.

Glycerol Phenyl Ether, $C_9H_{12}O_3$.—Phenol (23·5 grams) was mixed with α-monochlorohydrin (27·1 grams), and 10 grams of sodium hydroxide in 50 c.c. of water were added; a homogeneous liquid was formed, from which an oil separated on heating. The reaction was completed by heating for two hours on a water-bath. The whole was then shaken with ether and dilute aqueous sodium hydroxide; most of the glycerol phenyl ether seems to be extracted by the ether under these conditions. The ethereal solution was dried over potassium carbonate, the ether was evaporated, and the oil distilled under diminished pressure. On redistilling, a colourless oil was obtained, boiling at 194°/21 mm. (corr.) and solidifying on keeping. This was recrystallised from a mixture of ether and light petroleum, then twice from ether; the colourless crystals obtained melted at 55° (corr.) (Fourneau gives b. p. 200°/22 mm., m. p. 69°). (Found, C = 64·54; H = 7·19. Calc., C = 64·25; H = 7·20 per cent.)

The ether was also prepared by heating 6·45 grams of phenyl glycide ether with 0·8 gram of water in a sealed tube to 180° for twelve hours. Nearly all the water had disappeared, and the oil was brown in colour. After distillation and one recrystallisation from light petroleum crystals were obtained melting at 54—55° [equation (4)].

Glycerol o-Tolyl Ether, $C_{10}H_{14}O_3$.—Equimolecular proportions of *o*-cresol, α-monochlorohydrin, and sodium hydroxide were treated as described above. After heating, the mixture was extracted with benzene and washed with aqueous sodium hydroxide. The solution was dried over anhydrous potassium carbonate, the benzene evaporated, and the reddish-brown liquid obtained was distilled under diminished pressure. After two distillations a colourless oil was obtained, boiling at 195—196°/16 mm. (corr.). This solidified on keeping, and was recrystallised from a mixture of ether and light petroleum, then twice from ether. The product melted at 67° (corr.). Schivkovitch (*loc. cit.*) gives 66°.

The substance is soluble in ether, alcohol, or boiling water, but the oil which separates from the aqueous and alcoholic solutions does not readily crystallise. (Found, C=65·86; H=8·16. Calc., C=65·90; H=7·75 per cent.)

Glycerol m-*Tolyl Ether*, $C_{10}H_{14}O_3$.—It was found that anhydrous calcium chloride is not suitable for drying solutions of these substances. The reaction mixture was extracted with benzene, and after removing the benzene from the dried and purified solution, the oil was fractionated three times under diminished pressure.

On re-distilling, the boiling point was unchanged, and this, coupled with the results of analysis, was taken as evidence of the purity of the body. B. p. 198·5°/15·5 mm. (corr.); m. p. 60° (corr.). (Schivkovitch, *loc. cit.*, gives 65°.) (Found, C=66·04; H=7·94. Calc., C=65·90; H=7·75 per cent.)

Glycerol p-*Tolyl Ether*, $C_{10}H_{14}O_3$.—On keeping, the reaction mixture crystallises. The mass was washed with water, and some oil was collected (this oil crystallised on keeping, and probably consisted mainly of the ether). The main portion was recrystallised three times from ether, when it separated in glistening plates melting at 71·5° (corr.). (Schivkovitch gives 73—74°.) (Found, C=66·09; H=7·76. Calc., C=65·90; H=7·75 per cent.)

The ether is soluble in alcohol, from which it does not crystallise readily, ether, boiling benzene, boiling light petroleum, or boiling water, from which an oil separates on cooling, crystallising on keeping.

Glycerol s-*Tribromophenyl Ether.*—The reaction mixture was dissolved in much ether, and the solution was washed with aqueous sodium hydroxide. After evaporation of the ether the substance was recrystallised twice from alcohol, when it was obtained in microscopic prisms melting at 103·5—104·5° (corr.), sparingly soluble in cold alcohol, very soluble in boiling alcohol, moderately so in ether, benzene, hot light petroleum, or hot water, crystallising from the latter on cooling:

0·1594 gave 0·2230 AgBr. Br=59·54.

$C_9H_9O_3Br_3$ requires Br=59·23 per cent.

Glycerol Thymyl Ether.—In this case 18·7 grams of thymol were mixed with 5 grams of sodium hydroxide dissolved in 5 c.c. of water, and 11 grams of α-monochlorohydrin were added, an almost immediate separation of sodium chloride occurring. The mixture was left in the cold for some time, and the solid mass resulting was extracted with ether, the solution washed with aqueous sodium hydroxide, dried over anhydrous potassium carbonate, the ether evaporated, and the oil remaining was distilled under diminished pressure. The yield was 55 per cent.

After two fractionations an oil boiling at 210·5°/21 mm. (corr.) was obtained, which crystallised on keeping. The substance separates from solution in light petroleum as an oil, which crystallises in woolly masses, forming finally a waxy solid melting at 57° (corr.). It is soluble in hot water, alcohol, ether, or light petroleum:

0·2152 gave 0·5491 CO_2 and 0·1726 H_2O. C=69·59; H=8·98.

$C_{13}H_{20}O_3$ requires C=69·59; H=8·99 per cent.

Glycerol carvacryl ether boils at 215°/20 mm. (corr.), and solidifies on keeping. An alcoholic solution of the substance did not deposit crystals when cooled in a freezing mixture of ice and salt. Acetone, ether, a mixture of ether and light petroleum, chloroform, and carbon disulphide dissolve the substance, but crystallisation does not take place until all the solvent has disappeared, when the substance melts at 42—44° (corr.):

0·2162 gave 0·5490 CO_2 and 0·1772 H_2O. C=69·25; H=9·17.

$C_{13}H_{20}O_3$ requires C=69·59; H=8·99 per cent.

Glycerol Guaiacyl Ether.—The whole reaction mixture is soluble in water, ether extracts only a very small proportion of the oil, but benzene is more satisfactory.

After two fractionations under diminished pressure, an oil was obtained, boiling at about 215°/19 mm.; this solidified on keeping, and was recrystallised from ether and washed with light petroleum. Minute, rhombic prisms melting at 78·5—79° (corr.) separated, which were insoluble in boiling light petroleum, sparingly soluble in ether, moderately so in benzene, very soluble in alcohol or boiling water:

0·1924 gave 0·4254 CO_2 and 0·1234 H_2O. C=60·30; H=7·18.

$C_{10}H_{14}O_4$ requires C=60·57; H=7·12 per cent.

Glycerol α-Naphthyl Ether, $C_{13}H_{14}O_3$.—The reaction mixture was extracted with ether, and the solution washed with aqueous sodium hydroxide. Crystals separated from the ethereal solution, and these were removed and recrystallised from alcohol several times. The substance forms white, silvery scales melting at 95° (corr.). (Schivkovitch gives 91—92°.) (Found, C=71·76; H=6·54. Calc., C=71·52; H=6·47 per cent.)

*γ-Chloro-β-hydroxy-α-*m*-tolyloxypropane.*—This was prepared as described by Boyd and Marle (Trans., 1910, **97**, 1789), using 1/40th molecular proportion of sodium hydroxide in 20 per cent. aqueous solution. The mixture was extracted with ether after fifty-six days. Practically the whole boiled between 161° and 170°/

15 mm., and the yield of crude chlorohydrin was 67·5 per cent. of the theoretical. After three fractionations a colourless oil was obtained, boiling at 167·5°/13 mm. (corr.):

0·1882 gave 0·1348 AgCl. Cl=17·72.

$C_{10}H_{13}O_2Cl$ requires Cl=17·68 per cent.

The *phenylurethane*, prepared by mixing 5 grams of γ-chloro-β-hydroxy-*α*-*m*-tolyloxypropane with 3 grams of phenylcarbimide, heating to the boiling point of the mixture, and leaving at the ordinary temperature for nine days, is a white, crystalline solid. After crystallisation twice from alcohol and once from pure ether, it melted at 108—108·5° (corr.):

0·4758 gave 18·4 c.c. N_2 (moist) at 14° and 770 mm. N=4·61.

$C_{17}H_{18}O_3NCl$ requires N=4·38 per cent.

*γ-Chloro-β-hydroxy-α-*s*-tribromophenoxypropane.*—Owing to the sparing solubility of the sodium salt of tribromophenol in epichlorohydrin, an attempt to prepare this "chlorohydrin" in the usual way was not a success; in the presence of alcohol, however, the reaction proceeds normally. After forty-nine days the solid mass remaining was extracted with ether and washed with aqueous sodium hydroxide. On evaporation of the ether the residue crystallised, but it was not quite free from oil. The substance was recrystallised from dilute alcohol, then twice from light petroleum, when it melted at 49·7° (corr.):

0·1728 gave 0·2874 AgBr+AgCl; if AgBr:AgCl=3:1, Cl=8·35, Br=56·42.

$C_9H_8O_2ClBr_3$ requires Cl=8·38; Br=56·64 per cent.

The *phenylurethane* was obtained by adding 1·4 grams of phenylcarbimide to 4·8 grams of the "chlorohydrin" and warming. After twenty-four hours at the ordinary temperature the whole was solid; after thirteen days it was recrystallised twice from alcohol, then from pure ether, when it melted at 122·5° (corr.):

0·7309 gave 18·2 c.c. N_2 (moist) at 15·5° and 764 mm. N=2·92.

0·1796 „ 0·2332 AgBr+AgCl; if AgBr:AgCl=3:1, Cl=6·52, Br=44·05.

$C_{16}H_{13}O_3NClBr_3$ requires N=2·58; Cl=6·54; Br=44·21 per cent.

*γ-Chloro-β-hydroxy-α-*p*-nitrophenoxypropane.*—*p*-Nitrophenol and its sodium derivative are only very sparingly soluble in epichlorohydrin, and the reaction proceeds slowly, so that 20 c.c. of alcohol were added to a mixture of 34·7 grams of *p*-nitrophenol, 23 grams of epichlorohydrin, and 0·5 gram of sodium hydroxide (1/20th molecular equivalent) in 3 c.c. of water. After thirty days much unchanged *p*-nitrophenol remained, so that 11 grams of epichlorohydrin and a little alcohol were added.

After forty-eight days altogether the supernatant oil was poured away from the yellow, crystalline residue, dissolved in ether, and shaken with aqueous sodium carbonate. On evaporating the ether, a dark brown oil remained, which was treated with concentrated hydrochloric acid, and heated on the water-bath for two hours; it was then extracted with ether, the solution dried, evaporated, and the oil cautiously distilled under diminished pressure. A brown, very viscous liquid was obtained, which boiled at 241—242°/15 mm. (corr.):

0·6627 gave 0·4125 AgCl. Cl = 15·40.

$C_9H_{10}O_4NCl$ requires Cl = 15·31 per cent.

The *phenylurethane* is sparingly soluble in ether, but readily so in boiling alcohol, from which it separates almost completely on cooling. After several recrystallisations from alcohol it was obtained in rhombic crystals melting at 117·2° (corr.):

0·4196 gave 28·3 c.c. N_2 (moist) at 13° and 760 mm. N = 7·97.

$C_{16}H_{15}O_5N_2Cl$ requires N = 7·99 per cent.

γ-Chloro-β-hydroxy-α-thymoxypropane.—The preparation of the aryl ethers of glycerol-α-monochlorohydrin in the case of the phenols thymol, carvacrol, and guaiacol was rendered more difficult by the following circumstances: (1) These three phenols are extracted by ether, and to a less extent by light petroleum, from their aqueous solution, even in the presence of a large excess of sodium hydroxide. The complete removal of the phenol from the reaction mixture by treatment with aqueous sodium hydroxide is consequently difficult,* and the removal of the phenol by fractional distillation under diminished pressure is a slow process, and results in a very small yield of an impure product. (2) The reaction between the "chlorohydrins" and sodium hydroxide takes place much more readily in these cases than it does with the corresponding compounds of phenol and the cresols; thus thymol "chlorohydrin" prepared in the usual way gave Cl = 13·18 per cent.; after shaking with aqueous sodium hydroxide the same specimen gave Cl = 12·62 per cent. (Calc., Cl = 16·37 per cent.)

The corresponding compound of guaiacol reacts even more readily with sodium hydroxide; thus, 2·24 grams of nearly pure guaiacol "chlorohydrin," when shaken for a few minutes with 25 c.c. of 1·5*N*-sodium hydroxide, reacted to the extent of about 8 per cent., as shown by titration of the excess of sodium hydroxide with standard acid. That the deficiency of chlorine is due to the presence of glycide ether is indicated by the fact that the specimens do not appear to contain any of the phenol, and the addition of concentrated hydrochloric acid causes a rise of temperature; moreover, this treatment with hydrochloric acid results in the formation of "chlorohydrins" having the correct chlorine content. (3) In consequence of the ease with which these "chlorohydrins" react with sodium hydroxide, a little glycide ether is bound to be formed during the usual method of preparation, and this is further evidenced by the fact that a separation of sodium chloride takes place. It is extremely likely that the same takes place in the case of phenol and the cresols, but distillation in the latter cases seems to remove the small quantity of glycide ether quite satisfactorily; with thymol, carvacrol, and guaiacol, however, repeated distillation has little effect; thus, after five fractionations analysis gave Cl = 13·11 per cent. in the thymol derivative (Calc., Cl = 14·62 per cent.).

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* Practically a continued treatment with a very great excess of sodium hydroxide reduces the phenol to a negligible quantity, but the method is inconvenient for the reason following in (2).

Again, the guaiacol derivative, prepared without any attempt to remove the phenol by the use of sodium hydroxide, but freed from guaiacol by distillation, gave Cl = 15·97 per cent. (Calc., Cl = 16·37 per cent.).

The method adopted in the case of these three phenols was to heat the crude "chlorohydrin" for two hours on a water-bath with concentrated hydrochloric acid, extract with ether, wash with water, dry the solution with anhydrous calcium chloride, and, after evaporation of the ether, fractionate under diminished pressure. This method is open to the objection that there is a possibility of the formation of the isomeric γ-chloro-β-aryloxy-α-hydroxypropane [equation (7)]. That the quantity of this substance produced, if any, is very small is indicated by the following considerations: (1) Epichlorohydrin when treated with hydrogen chloride gives α-dichlorohydrin (Beilstein). (2) γ-Chloro-β-hydroxy-α-phenoxypropane, prepared from the glycide ether, was obtained in good yield (about 78 per cent.), and with the same boiling point as the specimen prepared by the direct method. Crude thymol "chlorohydrin" boiling at 188°/22 mm. (uncorr.) gave a "phenylurethane" melting at 107·5°; prepared from the glycide ether, the "chlorohydrin" boiled at 179·5°/14·5 mm. (uncorr.), and gave a "phenylurethane" melting at 107°. No evidence was obtained of any other "phenylurethane." Pure *m*-tolyl "chlorohydrin" prepared directly boiled at 167·5°/15 mm. (corr.), and gave a "phenylurethane" melting at 108—108·5°. When prepared from the glycide ether, the "chlorohydrin" boiled at 167·5°/14·5 mm. (corr.), and gave a "phenylurethane" melting at 107·5—108·5°. No evidence of another "phenylurethane" was obtained.

Thus the amount of the isomeric "chlorohydrin" produced (if any) must be very small, and the error introduced by converting the small quantity of glycide ether present in the crude "chlorohydrin" by means of hydrogen chloride is negligible.

Even this method fails, however, in the case of thymol, and the failure is probably to be attributed to the presence in the crude product of a small quantity of the glycerol dithymyl ether, which cannot be removed by hydrochloric acid; thus, before treatment with hydrochloric acid the crude substance gave Cl = 13·22 per cent., and after treatment 13·40 per cent.

Consequently the thymol "chlorohydrin" described was prepared by the action of concentrated hydrochloric acid on thymyl glycide ether. It is a colourless, viscous oil, boiling at 181·5°/14·5 mm. (corr.):

0·2406 gave 0·1408 AgCl. Cl = 14·48.

$C_{13}H_{19}O_2Cl$ requires Cl = 14·62 per cent.

The *phenylurethane* forms needles melting at 107·5° (corr.):

0·2211 gave 0·0885 AgCl. Cl = 9·90.

0·2449 „ 7·90 c.c. N_2 (moist) at 17·5° and 771 mm. N = 3·79.

$C_{20}H_{24}O_3NCl$ requires Cl = 9·80; N = 3·87 per cent.

γ-Chloro-β-hydroxy-α-carvacroxypropane.—Carvacrol (30 grams) and epichlorohydrin (23 grams) were added to a solution of sodium hydroxide (0·5 gram) in water (1·25 c.c.). The mixture was left for fifteen days, then extracted with ether, the solution washed with water, dried over calcium chloride, and after evaporation of the ether, distilled under diminished pressure. The yield was 17·3 grams (33 per cent.).

The product, which boiled at 181—183°/12·5 mm. (corr.), was heated on a water-bath for two hours with concentrated hydrochloric acid; it was then extracted with ether, the solution washed with water, dried, and distilled. The resulting oil boiled at 182·5°/13·5 mm. (corr.). On keeping for two months it formed a waxy solid melting at 35—36° (corr.):

0·2120 gave 0·1239 AgCl. Cl = 14·46.

$C_{13}H_{19}O_2Cl$ requires Cl = 14·62 per cent.

The *phenylurethane* forms colourless crystals melting at 92·25° (corr.).

γ-Chloro-β-hydroxy-α-guaiacyloxypropane.—After remaining for two months the reaction mixture still contained a quantity of guaiacol, so that a further half equivalent of epichlorohydrin was added, and the whole was extracted with ether a fortnight later.

The ethereal solution was washed with water only and dried over calcium chloride, and under these conditions the yield of crude "chlorohydrin," which boiled at 185·5°/14 mm. (corr.), was about 66 per cent. This was next heated with concentrated hydrochloric acid for two hours on the water-bath, and after extraction with ether an oil was obtained boiling at 183°/15 mm.:

0·5529 gave 0·3649 AgCl. Cl=16·33.

$C_{10}H_{13}O_3Cl$ requires Cl=16·37 per cent.

The *phenylurethane* melts at 120·5° (corr.):

0·3482 gave 12·9 c.c. N_2 (moist) at 20·5° and 769 mm. N=4·27.

$C_{17}H_{18}O_4NCl$ requires N=4·17 per cent.

γ-Chloro-β-hydroxy-α-1-naphthoxypropane.—The crude oil boils at about 230°/15 mm., and at this temperature the substance is decomposed with evolution of hydrogen chloride and the formation of a crystalline substance which does not contain chlorine.

I wish to express my thanks to Dr. Boyd for the interest which he has shown during the progress of this work.

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XXXIX.—*The Direct Esterification of Saturated and Unsaturated Acids.*

By EBENEZER REES THOMAS and JOHN JOSEPH SUDBOROUGH.

PREVIOUS researches on the catalytic esterification of organic acids (Trans., 1898, **73**, 82; 1899, **75**, 467; 1904, **85**, 534; 1905, **87**, 1840; 1907, **91**, 1033; 1908, **93**, 210; 1909, **95**, 315, 975) have proved that the rate of esterification by the catalytic method is largely influenced by the constitution of the acid. Substituents in the α-positions in the acetic, succinic, and acrylic acid series and in the ortho-position in the benzoic series produce a retardation in the rate of esterification,* and an olefine or acetylene linking in the αβ-position with respect to the carboxylic group has a most pronounced inhibiting effect. An α-carbonyl group, as in pyruvic and phenylglyoxylic acids (Kailan, *Monatsh.*, 1907, **28**, 1187; Sudborough, *Trans. Faraday Soc.*, 1912, **8**), also has a retarding influence, but the effect of the αβ-unsaturated linking between carbon and oxygen is not nearly so pronounced as an αβ-unsaturated linking between carbon and carbon.

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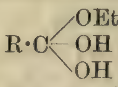
* Recent experiments tend to show that *o*-acetylbenzoic acid is esterified more readily than benzoic acid by the catalytic method.

Numerous investigations have also been made on the rates of esterification of organic acids when the direct method is used, that is, when the acid reacts with the alcohol in the absence of a catalyst. Menschutkin (*J. pr. Chem.*, 1881, [ii], **24**, 89; 1882, [ii], **25**, 193) claimed that his results proved that in the case of aliphatic acids the introduction of alkyl groups in close proximity to the carboxylic group lowers the rate of esterification and also that an olefine linking produces a retardation.

Objections have been raised to some of Menschutkin's numbers, as even during the short time (one hour) that the mixtures were heated equilibrium had been attained in several cases.

Lichty's results for the chloroacetic acids (*Amer. Chem. J.*, 1895, **17**, 27; 1896, **18**, 590) prove, on the other hand, that the introduction of chlorine atoms into the acetic acid molecule accelerates the direct esterification of the acid. This is exactly opposite to what is observed when the catalytic method is adopted. Sudborough and Lloyd (Trans., 1899, **75**, 467) and Gyr (*Ber.*, 1908, **41**, 4316) have proved that halogen substituents in the acetic acid molecule have an inhibiting effect when the catalytic method of esterification is used. Similar, but not such pronounced, differences have been met with in the case of aromatic acids (Rosanoff and Prager, *J. Amer. Chem. Soc.*, 1908, **30**, 1895; Michael and Oechslin, *Ber.*, 1909, **42**, 317), and both Rosanoff and Michael claim that their results vitiate the "steric hindrance" hypothesis of Victor Meyer. Michael has elaborated a view according to which the direct and catalytic methods are essentially different processes. The direct process consists in the formation of "Kekulé double molecules" between acid and alcohol, then the rearrangement of the chemical forces so that a derivative of an ortho-acid,  $R{\cdot}C(OEt)(OH)OH$, is formed (Henry, *Ber.*, 1877, **10**, 2041), and finally the decomposition of this complex into ester and water owing to the better "neutralisation of the atoms." The introduction of alkyl groups into acetic acid causes a diminution in the "free chemical energy" of the carboxyl group; the introduction of chlorine atoms, on the other hand, increases the energy contents of the carboxyl group, and hence increases its reactivity towards alcohol. Catalytic esterification consists in the formation of a complex between the alcohol and catalyst; the "double molecules" so formed have a greater energy content than the alcohol molecules alone, and hence can more rapidly bring about the state of maximum entropy in the acid-alcohol-catalyst system, that is, the formation of ester and water. Addition to the carbonyl group does not take place owing to the negative character of the alcohol-catalyst double molecule, but the acid is added on to the original double molecule, giving a more complex double molecule, which is directly transformed into ester, water, and catalyst.

Our own view is that the direct and catalytic esterification are essentially the same, the only difference being that in the former case the organic acid is its own catalyst. As the activity of the catalyst is largely a function of its strength (Goldschmidt), it follows that a strong organic acid will be esterified more rapidly than a feeble acid by the direct method unless some powerful inhibiting factor comes into play; thus di- and tri-chloroacetic acids are esterified more rapidly than acetic acid. In none of the cases examined by Rosanoff and Prager and by Michael and Oechslin is an ortho-substituted benzoic acid esterified more rapidly than benzoic acid by the direct method, although many of them are much stronger acids. This may be due to the inhibiting effect of the ortho-substituents.

An interesting acid to study in this connexion would be one of the type of *αα*-dichloroglutaric acid, $\underset{(1.)}{CO_2H}\cdot CCl_2\cdot CH_2\cdot CH_2\cdot \underset{(2.)}{CO_2H}$. According to Michael's view the carboxylic group 1 should be more readily esterified than carboxylic group 2 by the direct method, whereas by the catalytic method the carboxylic group 2 should be the more easily converted into the carbethoxy-group. According to our view, carboxyl No. 2 should be esterified more readily than No. 1 by both catalytic and direct methods, as in the direct method the function of the carboxylic group No. 1 is chiefly to act as catalyst. Our intention is to study the esterification of such acids by different methods, and to examine the acid esters formed.

Most of the results which have been obtained by the catalytic and direct methods are in harmony with the view that in both processes at least two factors are concerned, namely, (1) the strength of the acid esterified, (2) a stereochemical factor, for example, the presence of substituting groups in close proximity to the carboxyl group. In the direct method the first factor is of paramount importance, but the second factor comes into play especially in the aromatic series. When the catalytic method is used, the first factor is almost negligible, as the catalyst is a strong acid and completely overpowers the catalysing influences of the carboxylic acids themselves (compare Sudborough and Feilmann, Proc., 1897, **13**, 241).

The object of the experiments described in this paper has been to ascertain whether when the direct method of esterification is employed the same differences between the rates of esterification of saturated and unsaturated acids are observed as when the catalytic method is used. The only data bearing on this point are Menschutkin's results with crotonic acid and Michael and Oechslin's comparison of crotonic and *n*-butyric acids (*Ber.*, 1909, **42**, 322), which indicate that an *αβ*-olefine linking has a retarding effect on direct esterification.

Our method of procedure was to heat a known weight of the acid with a large excess of pure methyl alcohol in sealed tubes at 100° for given periods of time, and to estimate the amount of ester by titrating the unesterified acid by means of standard alkali.

The results we have obtained are given in the following table, which also gives the dissociation constants of the different acids where these are known.

Velocity constants have not been determined, as when the direct method is used in the presence of a large excess of alcohol the ordinary equation for a unimolecular reaction does not hold good; the values for k calculated from $k=1/t\log a/a-x$ diminish as t increases.

No.	Acid.	Formula.	Percentage esterified. Each number is the mean of two experiments.			Dissociation constant.
			24 hours.	72 hours.	144 hours.	$k\times10^5$.
1.	Cinnamic	$CHPh:CH\cdot CO_2H$	2·2	7·2	13·6	3·5
2.	*β*-Phenylpropionic	$CH_2Ph\cdot CH_2\cdot CO_2H$	18·2	29·9	56·4	2·3
3.	*βγ*-Phenylcrotonic	$CHPh:CH\cdot CH_2\cdot CO_2H$	39·4	65·4	—	—
4.	Crotonic	$CHMe:CH\cdot CO_2H$	1·4	4·2	7·4	2·0
5.	*n*-Butyric	$CH_2Me\cdot CH_2\cdot CO_2H$	9·0	22·8	35·7	1·5
6.	*iso*Butyric	$CHMe_2\cdot CO_2H$	7·5	19·0	30·8	1·44
7.	*β*-Ethylacrylic	$CH_2Me\cdot CH:CH\cdot CO_2H$	0·8	5·1	9·3	1·48
8.	Ethylidenepropionic	$CHMe:CH\cdot CH_2\cdot CO_2H$	22·6	48·2	64·3	3·35
9.	Allylacetic	$CH_2:CH\cdot CH_2\cdot CH_2\cdot CO_2H$	10·9	25·3	41·2	2·09
10.	*n*-Valeric	$CH_2Me\cdot CH_2\cdot CH_2\cdot CO_2H$	13·0	31·0	45·7	1·58
11.	*β*-Dimethylacrylic	$CMe_2:CH\cdot CO_2H$	0·6	1·0	2·0	—
12.	*iso*Valeric	$CHMe_2\cdot CH_2\cdot CO_2H$	4·6	10·8	19·4	1·73
13.	*β*-Propylacrylic	$CH_2Me\cdot CH_2\cdot CH:CH\cdot CO_2H$	3·3	8·6	15·4	1·89
14.	Hydrosorbic	$CH_2Me\cdot CH:CH\cdot CH_2\cdot CO_2H$	16·9	38·0	55·6	2·5
15.	Sorbic	$CHMe:CH\cdot CH:CH\cdot CO_2H$	2·9	6·4	10·9	1·73
16.	*n*-Hexoic	$CH_2Me\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO_2H$	10·2	25·0	38·6	1·44
17.	*iso*Butylacetic	$CHMe_2\cdot CH_2\cdot CH_2\cdot CO_2H$	10·8	25·7	39·9	1·44
18.	Methyl hydrogen maleate	$CO_2H\cdot CH:CH\cdot CO_2Me$	21·8	40·9	58·2	600
19.	Methyl hydrogen succinate	$CO_2H\cdot CH_2\cdot CH_2\cdot CO_2Me$	11·3	28·4	47·3	3·3
20.	Phenylpropylideneacetic	$CH_2Ph\cdot CH_2\cdot CH:CH\cdot CO_2H$	0·5	5·5	—	—
21.	Cinnamenylpropionic	$CHPh:CH\cdot CH_2\cdot CH_2\cdot CO_2H$	12·5	30·7	—	—

The results obtained point to the following general conclusions:

(1) Where the difference in the strengths of the acids is not very marked, the *αβ*-unsaturated acid is esterified less readily than its saturated analogue, although, as a rule, the unsaturated acid is a

slightly stronger acid than the saturated compound (Nos. 1 and 2, 4 and 5, 7 and 10, 11 and 12, 13 and 16).

When the difference in the strengths of the two acids is very pronounced, as in the case of methyl hydrogen maleate and methyl hydrogen succinate, where the unsaturated acid is nearly two hundred times as strong as its saturated analogue, the unsaturated acid reacts more readily than the saturated (Nos. 18 and 19).

(2) Acids with the olefine linking in the $\beta\gamma$-position are more readily esterified than the corresponding saturated acids (Nos. 3 and 2, 8 and 10, 14 and 16). The $\beta\gamma$-acids are, as a rule, stronger than either the saturated analogues or the $\alpha\beta$-isomerides (compare Fichter and Pfister, *Annalen*, 1904, **334**, 201; Fichter and Müller, *ibid.*, 1906, **348**, 256; Fichter and Rudin, *Ber.*, 1904, **37**, 1615; Fichter and Obladen, *ibid.*, 1909, **42**, 4703).

(3) When the olefine linking is still further removed from the carboxylic group, its effect on the rate of esterification is not marked. The two $\gamma\delta$-unsaturated acids examined (Nos. 9 and 21) are esterified at much the same rate as saturated acids.

(4) Only one acid with conjugate double linkings, one of which is in the $\alpha\beta$-position, has been examined, sorbic acid (No. 15), and in this case the effect is much the same as a simple $\alpha\beta$-double linking.

(5) Normal acids, both saturated and unsaturated, are generally more readily esterified than the isomerides containing branching chains (Nos. 5 and 6, 7 and 11, 10 and 12). When, however, this branching is not in close proximity to the carboxylic group its effect is very small (Nos. 16 and 17).

(6) Although an $\alpha\beta$-unsaturated acid is esterified less readily than its saturated analogue by the direct method, the difference is not nearly so marked as when the catalytic method is used. In the latter case the ratio is frequently 1:40, but using the direct method the ratio is often 1:4 or 1:5.

EXPERIMENTAL.

The tubes used in the experiments were made of hard Jena-glass 1 cm. internal diameter. After thoroughly cleaning and drying, each tube was drawn out at either end, one end was sealed and the other fitted with a rubber tube and glass plug. Each tube was fixed in a wire cage, by means of which it was suspended on the balance, and also subsequently hung in the bath. The alcohol used in all the experiments was Kahlbaum's No. 1 methyl alcohol, which was distilled five times over small amounts of calcium.

About 0·01 gram-molecule of the acid was weighed out into a small flask and about one hundred and twenty-six times the theoretical weight of pure methyl alcohol added, and the weight of the solution determined. With concentrations of this type it was found that all the acids dissolved at the ordinary temperature, and with such a large excess of alcohol the concentration of the alcohol can be regarded as remaining constant. About three grams of such a solution was transferred to each tube, and the whole weighed and then sealed.

To transfer the solution, the flask was fitted with a rubber cork carrying two tubes; the longer tube was drawn out to a fine capillary 1·5 cm. long, and the other provided with a calcium chloride tube and blow ball, so that the solution driven out of the flask was replaced by dry air. Each tube was re-weighed, and sealed off without allowing the flame to come in contact with the open end of the tube. The tubes were placed in wire cages, and suspended from long brass rods in boiling water contained in large cans provided with reflux condensers.

In all cases at least two determinations were made, and preliminary experiments showed that results agreeing to within 4 or 5 per cent. could be obtained. In many cases where it was desired to compare two acids, the tubes containing the different solutions were heated side by side for the same length of time, so that the results are strictly comparable. The results obtained by heating a given acid solution for the same periods, but at different times, were also in excellent agreement, so that all the results are directly comparable.

The concentration of the acid solution before heating was determined by titration with barium hydroxide solution, using phenolphthalein as indicator. In all cases, with the exception of volatile acids (such as butyric and valeric), the concentration determined by titration agreed with the amount weighed. With the volatile acids the actual concentration used in the calculations was that determined by titration.

After the tubes have been heated for the stated periods, they were removed, and at once plunged into cold water. The outside of the tube was then well washed, the tube opened, and the contents washed into a titration flask by means of neutral * rectified spirits. Freshly boiled distilled water was added, and the amount of free acid determined by titration with standard barium hydroxide solution.

The results obtained were in most cases in good agreement. In one experiment with each of the acids, valeric, *iso*valeric, and

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* The alcohol used was mixed with sufficient baryta water until, when mixed with water and two drops of phenolphthalein, a single further drop of alkali gave a pink coloration.

β-ethylacrylic, remarkable results were obtained. After heating the two former for seventy-two hours and the last for one hundred and forty-four hours, titrations indicated that almost complete esterification had taken place. These results may have been due to the presence of a minute trace of some catalyst in the tubes.

(1) *Cinnamic acid*, m. p. 133°, after crystallisation from benzene.

A. Weight of acid, 1·3036. Weight of solution, 36·82.
2·855 of solution (=0·1011 of acid) required 34·60 c.c. of 0·0198*N*-barium hydroxide solution (=0·1015 gram acid).

B. Weight of acid, 1·5330. Weight of solution, 43·17.
3·244 of solution (=0·1151 of acid) required 38·90 c.c. of 0·0198*N*-barium hydroxide (=0·1140 gram acid).

	Weight of solution.	*t*, in hours.	No. of c.c. of 0·0198*N*-barium hydroxide.	Per cent. esterified.
A.	2·876	24	34·05	2·3
	3·148	24	37·30	2·2
	3·146	48	35·60	6·6
	3·003	48	34·00	6·6
	2·805	72	31·30	7·9
	3·195	72	35·80	7·6
B.	2·761	72	31·10	6·1
	3·166	144	32·80	13·6
	3·674	144	38·10	13·5

(2) *β-Phenylpropionic acid*, m. p. 48·5—49·5°.

A. Weight of acid, 0·9770. Weight of solution, 27·9.
2·798 of solution (=0·0980 acid) required 32·95 c.c. of 0·0198*N*-barium hydroxide solution (=0·0979 acid).

B. Weight of acid, 0·8100. Weight of solution, 22·55.
2·959 of solution (=0·1062 acid) required 35·60 c.c. of 0·0198*N*-barium hydroxide (=0·1057 gram acid).

	Weight of solution.	*t*, in hours.	No. of c.c. of 0·0198*N*-barium hydroxide.	Per cent. esterified.
A.	3·051	24	29·40	18·3
	4·152	24	40·10	18·1
	2·891	48	24·20	29·0
	3·284	48	26·80	30·8
	4·373	72	31·70	38·5
	3·752	72	27·15	38·6
B.	4·166	144	22·30	55·6
	3·689	144	19·15	57·1

(3) *βγ-Phenylcrotonic acid*, m. p. 86°.

Weight of acid, 1·0162. Weight of solution, 26·26.

Weight of solution.	*t*, in hours.	No. of c.c. of baryta.	Concentration of barium hydroxide.	Per cent. esterified.
2·145	0	25·6	0·0198*N*	0
3·513	24	25·42	0·0198*N*	39·4
2·507	24	18·15	0·0198*N*	39·4
2·224	48	12·05	0·0198*N*	54·6
3·384	48	18·40	0·0198*N*	54·4
2·568	72	10·70	0·0198*N*	65·1
4·080	72	16·75	0·0198*N*	65·6

(4) *Crotonic acid*, m. p. 72°.

Weight of acid, 1·02. Weight of solution, 48·85.

Weight of solution.	*t*, in hours.	No. of c.c. of barium hydroxide.	Concentration of barium hydroxide.	Per cent. esterified.
3·010	0	38·15	0·01905*N*	0
3·272	24	40·70	0·01905*N*	1·1
2·872	24	35·75	0·01905*N*	1·7
3·157	72	38·45	0·01905*N*	3·9
3·212	72	38·90	0·01905*N*	4·4
4·021	144	47·20	0·01905*N*	7·4
4·067	144	47·80	0·01905*N*	7·3

(5) n-*Butyric acid*, b. p. 163·5°/757 mm.

Weight of solution.	*t*, in hours.	No. of c.c. of barium hydroxide.	Concentration of barium hydroxide.	Per cent. esterified.
4·175	0	52 00	0·01927*N*	0
2·166	0	27·15	0·01927*N*	0
4·287	24	48·70	0·01927*N*	9·0
4·023	24	45·75	0·01927*N*	9·0
2·995	72	28·80	0·01927*N*	23·0
2·996	72	28·95	0·01927*N*	22·7
3·671	144	29·75	0·01927*N*	35·1
4·172	144	33·30	0·01927*N*	36·1

(6) iso*Butyric acid*, b. p. 153—154·5°/765 mm.

Weight of solution.	*t*, in hours.	No. of c.c. of barium hydroxide.	Concentration of barium hydroxide.	Per cent. esterified.
3·216	0	39·95	0·01927*N*	0
2·466	0	30·75	0·01927*N*	0
3·698	24	42·55	0·01927*N*	7·5
3·073	24	35·43	0·01927*N*	7·4
2·823	72	28·50	0·01927*N*	18·9
2·689	72	27·10	0·01927*N*	19·0
3·747	144	32·30	0·01927*N*	30·8
3·737	144	32·20	0·01927*N*	30·7

(7) *β-Ethylacrylic Acid.*

This was prepared as described in Trans., 1911, **99**, 2314.

Weight of solution.	*t*, in hours.	No. of c.c. of barium hydroxide.	Concentration of barium hydroxide.	Per cent. esterified.
2·480	0	28·6	0·0198*N*	0
1·560	0	17·9	0·0198*N*	0
2·726	24	31·0	0·0198*N*	1·2
2·529	24	29·0	0·0198*N*	0·4
3·189	72	34·85	0·0198*N*	5·1
3·661	72	39·95	0·0198*N*	5·2
2·263	72	24·70	0·0198*N*	5·1
3·726	144	38·85	0·0198*N*	9·4
2·891	144	30·20	0·0198*N*	9·3

(8) *Ethylidenepropionic acid*, b. p. 191—192°/747 mm., was prepared from the barium salt (Trans., 1911, **99**, 2314).

Weight of solution.	*t*, in hours.	No. of c.c. of barium hydroxide.	Concentration of barium hydroxide.	Per cent. esterified.
3·209	0	38·6	0·1927*N*	0
3·586	0	43·4	0·1927*N*	0
3·311	24	30·80	0·1927*N*	22·9
3·004	24	28·15	0·1927*N*	22·3
3·721	72	23·15	0·1927*N*	48·4
3·807	72	23·85	0·1927*N*	48·1
4·392	144	19·00	0·1927*N*	64·1
3·910	144	16·80	0·1927*N*	64·4

(9) *Allylacetic acid*, b. p. 186·5—187·5°/770 mm.

Weight of solution.	*t*, in hours.	No. of c.c. of barium hydroxide.	Concentration of barium hydroxide.	Per cent. esterified.
2·457	0	28·8	0·0198*N*	0
1·200	0	14·05	0·0198*N*	0
3·155	24	33·00	0·0198*N*	10·8
3·866	24	40·35	0·0198*N*	11·0
3·217	72	27·90	0·0198*N*	25·9
4·288	72	37·85	0·0198*N*	24·7
4·216	144	29·05	0·0198*N*	41·2
4·124	144	28·47	0·0198*N*	41·1

(10) n-*Valeric acid*, b. p. 185·5—186·5°/766 mm.

Weight of solution.	*t*, in hours.	No. of c.c. of barium hydroxide.	Concentration of barium hydroxide.	Per cent. esterified.
3·080	0	37·25	0·0198*N*	0
2·353	0	28·55	0·0198*N*	0
3·131	24	32·80	0·0198*N*	13·4
2·804	24	29·65	0·0198*N*	12·7
4·905	72	41·60	0·0198*N*	30·0
3·517	72	28·95	0·0198*N*	32·0
3·880	144	25·80	0·0198*N*	45·1
5·176	144	34·60	0·0198*N*	44·8

(11) *β-Dimethylacrylic acid*, m. p. 67·8—68·3°.

Weight of solution.	*t*, in hours.	No. of c.c. of barium hydroxide.	Concentration of barium hydroxide.	Per cent. esterified.
3·668	0	44·60	0·0198*N*	0
3·440	24	41·50	0·0198*N*	0·8
3·443	24	41·70	0·0198*N*	0·4
3·378	72	40·70	0·0198*N*	0·9
3·744	72	45·10	0·0198*N*	1·0
1·881	144	22·50	0·0198*N*	1·6
4·374	144	51·90	0·0198*N*	2·4

(12) iso*Valeric acid*, b. p. 176—176·5°/768 mm.

Weight of solution.	*t*, in hours.	No. of c.c. of barium hydroxide.	Concentration of barium hydroxide.	Per cent. esterified.
3·386	0	41·40	0·0198*N*	0
4·848	24	56·60	0·0198*N*	4·5
3·228	24	37·60	0·0198*N*	4·7
2·899	72	31·60	0·0198*N*	10·9
3·673	72	40·10	0·0198*N*	10·7
3·992	144	39·35	0·0198*N*	19·4
3·352	144	33·05	0·0198*N*	19·4

(13) *β-Propylacrylic acid*, m. p. 32·1—32·3°.

Weight of solution.	*t*, in hours.	No. of c.c. of barium hydroxide.	Concentration of barium hydroxide.	Per cent. esterified.
2·284	0	28·00	0·01965*N*	0
2·703	24	32·00	0·01965*N*	3·6
2·391	24	28·45	0·01965*N*	3·1
2·590	72	29·05	0·01965*N*	8·5
2·175	72	24·45	0·01965*N*	8·5
2·755	144	28·60	0·01965*N*	15·5
2·197	144	22·85	0·01965*N*	15·2

(14) *Hydrosorbic acid*, b. p. 102—104°/9 mm.

Weight of solution.	*t*, in hours.	No. of c.c. of barium hydroxide.	Concentration of barium hydroxide.	Per cent. esterified.
4·875	0	58·50	0·01905*N*	0
2·955	0	35·40	0·01905*N*	0
3·742	24	37·25	0·01905*N*	17·0
4·456	24	44·55	0·01905*N*	16·7
3·847	72	28·65	0·01905*N*	37·9
4·658	72	34·65	0·01905*N*	38·0
3·426	144	18·60	0·01905*N*	55·7
3·581	144	19·15	0·01905*N*	55·4

(15) *Sorbic acid*, m. p. 133—134°.

Weight of solution.	*t*, in hours.	No. of c.c. of barium hydroxide.	Concentration of barium hydroxide.	Per cent. esterified.
3·573	0	44·95	0·01905*N*	0
3·601	0	45·30	0·01905*N*	0
3·719	24	45·25	0·01905*N*	3·2
3·396	24	41·60	0·01905*N*	2·6
3·532	72	41·85	0·01905*N*	5·8
3·695	72	43·22	0·01905*N*	7·0
4·004	144	44·60	0·01905*N*	11·4
4·340	144	48·95	0·01905*N*	10·4

(16) n-*Hexoic acid*, b. p. 202—202·5°/761 mm.

Weight of solution.	*t*, in hours.	No. of c.c. of barium hydroxide.	Concentration of barium hydroxide.	Per cent. esterified.
2·591	0	32·35	0·01905*N*	0
3·373	0	42·35	0·01905*N*	0
2·785	24	31·30	0·01905*N*	10·2
3·056	24	34·35	0·01905*N*	10·2
2·611	72	24·45	0·01905*N*	25·2
2·859	72	26·95	0·01905*N*	24·7
3·642	144	28·00	0·01905*N*	38·6

(17) iso*Butylacetic acid*, b. p. 197·5—198°/774 mm.

Weight of solution.	*t*, in hours.	No. of c.c. of barium hydroxide.	Concentration of barium hydroxide.	Per cent. esterified.
3·868	0	50·72	0·01905*N*	0
2·794	0	36·50	0·01905*N*	0
3·648	24	42·55	0·01905*N*	10·9
3·410	24	39·90	0·01905*N*	10·7
3·556	72	34·60	0·01905*N*	25·7
3·020	72	29·45	0·01905*N*	25·6
2·713	144	21·40	0·01905*N*	39·8
3·579	144	28·10	0·01905*N*	40·0

(18) *Methyl hydrogen maleate* (compare Trans., 1905, **87**, 1844).

Weight of solution.	*t*, in hours.	No. of c.c. of barium hydroxide.	Concentration of barium hydroxide.	Per cent. esterified.
3·827	0	43·15	0·0198*N*	0
3·398	0	38·25	0·0198*N*	0
3·750	24	32·95	0·0198*N*	21·9
3·690	24	32·55	0·0198*N*	21·7
4·035	72	26·75	0·0198*N*	41·1
2·742	72	18·80	0·0198*N*	40·7
4·456	144	21·00	0·0198*N*	58·2

(19) *Methyl hydrogen succinate*, m. p. 56·5—57·5°.

Weight of solution.	t, in hours.	No. of c.c. of barium hydroxide.	Concentration of barium hydroxide.	Per cent. esterified.
2·418	0	29·20	0·0198N	0
2·187	0	26·40	0·0198N	0
3·804	24	40·55	0·0198N	11·6
3·081	24	33·13	0·0198N	10·9
3·233	72	28·00	0·0198N	28·2
3·618	72	31·15	0·0198N	28·6
3·543	144	22·70	0·0198N	46·8
4·421	144	27·80	0·0198N	47·9

(20) *Phenylpropylideneacetic acid*, m. p. 102·5—103°.

Weight of solution.	t, in hours.	No. of c.c. of barium hydroxide.	Concentration of barium hydroxide.	Per cent. esterified.
4·274	0	51·60	0·01927N	0
2·789	0	33·55	0·01927N	0
2·107	24	25·10	0·01927N	1
3·310	24	39·85	0·01927N	0
3·560	72	40·50	0·01927N	5·5

(21) *Cinnamenylpropionic acid*, m. p. 89—90°.

Weight of solution.	t, in hours.	No. of c.c. of barium hydroxide.	Concentration of barium hydroxide.	Per cent. esterified.
3·281	0	39·50	0·01927N	0
2·406	0	29·00	0·01927N	0
3·127	24	33·00	0·01927N	12·5
3·272	24	34·55	0·01927N	12·4
2·677	72	22·30	0·01927N	30·9
2·578	72	21·60	0·01927N	30·5

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XL.—*The Quantitative Estimation of Hydroxy-, Amino-, and Imino-derivatives of Organic Compounds by means of the Grignard Reagent, and the Nature of the Changes taking place in Solution.*

By HAROLD HIBBERT.

Part I.—Experiments with Hydroxyl Compounds.

IN a recent paper Zerewitinoff (*Ber.*, 1910, **43**, 3590) has published a series of experiments on the quantitative estimation of the "reactive" hydrogen in organic compounds by means of the

Grignard reagent, an interesting feature of which is the employment of solvents other than amyl ether and pyridine for this purpose. This method was first developed qualitatively by Tschugaeff (*Ber.*, 1902, **35**, 3912), and then shown to be applicable from a quantitative point of view by the author, working in conjunction with Sudborough (Trans., 1904, **85**, 933), the chief advance in their contribution consisting in the substitution of amyl ether as solvent, instead of ethyl ether, whereby changes due to the vapour pressure of the solvent were largely eliminated. Zerewitinoff in his earlier publications (*Ber.*, 1907, **40**, 2023; 1908, **41**, 2233) by replacing amyl ether with pyridine was able, on account of the greater degree of solubility of organic compounds in the latter solvent, to extend the usefulness of the method to a much wider series of hydroxyl derivatives, such as, for instance, menthol, fluorescein, alizarin, vanillin, the sugars, oximes, etc.

In a later paper by Sudborough and the author (Trans., 1909, **95**, 477) the above method for estimating hydroxyl compounds was shown to be also applicable to the quantitative estimation of primary and secondary amines, the experimental evidence at that time available indicating that a primary or secondary amine on treatment with the Grignard reagent at the ordinary temperature liberated an amount of methane corresponding with one atom of hydrogen, and only on heating the solution to 120° was the second hydrogen atom of the primary amine capable of reacting. In this paper it was shown that phenetole could be substituted for amyl ether with advantage, since a larger number of organic derivatives are soluble in this solvent, a fact which Zerewitinoff in his recent communication (*Ber.*, 1910, **43**, 3590) appears to have overlooked. The latter author has now extended the method to the determination of the "reactive hydrogen" in various alkaloids and tautomeric substances, and has shown at the same time that other solvents, such as xylene, mesitylene, and anisole, may be substituted for amyl ether, phenetole, and pyridine. In view of the extended series of quantitative estimations already carried out in this connexion, all tending to establish its value as a trustworthy means of analysis, and further its introduction into the literature (Meyer-Tingle, "Estimation of Radicles in Organic Compounds"; Smedley, Trans., 1910, **97**, 1489; Sudborough and James, "Practical Organic Chemistry"), the author considers it advisable to publish at this stage some uncompleted work on this subject carried out by him in England some time ago, the results of which tend to disprove the idea of the general applicability of the method from a quantitative point of view. The incentive to the present research was found in the surprising result obtained in an attempt to estimate the amount of methyl alcohol present in a mixture of this with acetone, whereby it was found that only about 45 per cent. of the theoretical quantity of methane corresponding with the methyl alcohol present was evolved, the reaction being carried out in phenetole solution in the manner already described (Trans., 1904, **85**, 935). That this result was not due to the presence of the acetone was proven by carrying out a determination using pure methyl alcohol alone, with the following result:

Expt. 1.—0·0948 Gram of pure methyl alcohol gave 30·0 c.c. of methane at N.T.P. (theory requires 65·9 c.c.).

With ethyl and propyl alcohol the following figures were obtained in experiments carried out under similar conditions:

Expt. 2.—0·1402 Gram of anhydrous ethyl alcohol gave 48·2 c.c. of methane at N.T.P. (theory = 67·9 c.c.).

Expt. 3.—0·1118 Gram of anhydrous propyl alcohol gave 34·3 c.c. of methane at N.T.P. (theory = 41·4 c.c.).

Since *iso*amyl alcohol gives a normal value, at least in pyridine solution, the behaviour of the higher alcohols was not further investigated.

It is conceivable that the above results might be due to a secondary reaction of the type:

$$Mg(O{\cdot}CH_3)I + CH_3{\cdot}OH = CH_3{\cdot}O{\cdot}CH_3 + Mg(OH)I,$$

whereby an ether and magnesium hydroxyiodide would be formed, the latter substance possibly not reacting further with the Grignard reagent, so that a portion of the hydroxyl compound would in this way be removed from the sphere of action. This, however, is rendered very improbable by the fact that, first, no traces of mixed ethers could be found in the above cases, and secondly, when the magnesium derivatives from phenetole and *iso*amyl alcohol, namely, $Mg(O{\cdot}C_6H_5)I$ and $Mg(O{\cdot}C_5H_{11})I$, respectively, were heated with methyl or ethyl alcohol, no traces of anisole, phenetole, or the mixed *iso*amyl ethers could be detected. There remains the further question as to what extent the abnormal values for the lower fatty alcohols obtained above may be accounted for by the solubility of the methane in the solvent employed (phenetole), since in the previous communication of Sudborough and Hibbert (*loc. cit.*) the low values obtained in the quantitative estimation of various primary and secondary amines were ascribed to this cause.

The following two experiments, carried out under the same conditions, prove that these low values are not related in any way to the solubility of the methane, since a very considerable increase in the quantity of solvent employed is without effect on the amount of methane evolved.

Expt. 4.—0·2250 Gram of α-naphthol gave 31·1 c.c. of methane at N.T.P. (theory requires 34·7 c.c.). Volume of phenetole taken = 3 c.c.; volume of magnesium methyl iodide solution used = 7 c.c.

Expt. 5.—0·2250 Gram of α-naphthol gave 31·5 c.c. of methane at N.T.P. (theory requires 34·7 c.c.). Volume of phenetole taken = 10 c.c.; volume of magnesium methyl iodide solution used = 7 c.c.

A further series of determinations carried out with methyl, ethyl, propyl, and benzyl alcohols, α-naphthol, and tribromophenol in phenetole solution gave values as indicated in table I, approximately the same amount of solvent (phenetole) and Grignard reagent (considerable excess) being used for each determination.

TABLE I.

(*Experiments in Phenetole Solution.*)

No. of expt.	Substance.	Weight taken, grams.	Temperature.	Pressure, mm.	Vol. found, c.c.	Vol. measured at N.T.P.	Theoretical value, c.c.	CH_4 evolved, per cent.	Equilibrium factor = theor. value/exper. value, mean value.
6*A*	Methyl alcohol	0·0948	15·0°	769·0	31·3	30·0	65·9	45·5	2·3
6*B*		0·0634	12·0	771·0	18·5	18·0	44·1	40·5	
7*A*	Ethyl alcohol	0·1402	14·5	775·0	49·8	48·2	67·9	71·0	1·4
7*B*		0·0708	11·0	748·5	26·0	24·6	34·2	71·9	
8*A*	Benzyl alcohol	0·1854	12·0	770·3	31·9	31·0	38·2	81·1	1·2
8*B*		0·1030	11·0	750·5	19·7	18·7	21·2	88·2	
9*A*	α-Naphthol	0·2348	11·0	764·0	34·2	33·1	36·3	91·2	1·8
9*B*		0·1304	11·0	764·0	19·6	18·9	20·1	94·0	
10	Tribromophenol	0·5404	12·0	769·0	34·0	33·0	36·3	90·9	1·1
11	Propyl alcohol	0·1118	13·0	770·0	35·5	34·3	41·4	82·8	1·2

As indicated in the above figures we have apparently always the *same percentage* of methane evolved with the *same* hydroxyl compound, even when the amount of the latter, as in the case of ethyl alcohol quoted above, is increased by 100 per cent. The results would seem to justify the assumption that we are dealing in each case with some kind of a definite equilibrium in the solution, the nature of which varies with the character of the hydroxyl compound taken. In this connexion a so-called "equilibrium factor" equal to the ratio:

$$\frac{\text{Theoretical quantity of methane}}{\text{Quantity of methane found}}$$

has been calculated, to which reference will be made later. In view of the interesting nature of these results, two experiments with ethyl alcohol and α-naphthol respectively were carried out in amyl ether solution, using for this purpose a solution of magnesium methyl iodide in the same solvent.

Expt. 12.—0·1383 Gram of ethyl alcohol gave 48·8 c.c. of methane at N.T.P. (theory requires 66·9 c.c., that is, 72·9 per cent. was liberated).

There was no further increase on heating the solution for thirty minutes at 50—60°, nor even when heated for some time at 100°. We thus have the very interesting result that the percentage of methane evolved, namely, 73 per cent. of that demanded by theory, is identical with that obtained by working in phenetole solution (experiments 7*A* and 7*B*).

Expt. 13.—0·2668 Gram of α-naphthol gave 41·2 c.c. of methane at N.T.P. (theory requires 41·2 c.c.).

α-Naphthol thus reacts in amyl ether solution to give a theoretical yield, confirming in this respect the earlier work published on this subject, in which, unfortunately, exclusively aromatic hydroxy-compounds were investigated. Apparently, therefore, whilst the lower fatty alcohols also react in amyl ether solution abnormally, the aromatic derivatives react to give approximately theoretical values. In this connexion it must be pointed out that the aromatic derivatives in general yield magnesium derivatives which are insoluble in amyl ether, the derivatives of the lower fatty alcohols being more soluble, whilst in phenetole both the aromatic and fatty hydroxy-compounds yield magnesium derivatives readily soluble in this solvent, and it is doubtless due to this fact that we do not get with the aromatic derivatives in amyl ether an equilibrium of the nature indicated in the previous experiments (table I). Not only is it true that in amyl ether (as contrasted with phenetole) do we get approximately theoretical values for the amount of methane evolved by hydroxy-compounds (apart from the lower fatty alcohols), but these derivatives may also be estimated with a fair degree of accuracy in various mixtures of them with other organic substances, as indicated in experiments 14, 15, and 16 (table II).

TABLE II.

Estimation of Hydroxy-compounds in Mixtures (Amyl Ether Solution).

No. of expt.	Mixture.	Weight of hydroxy derivative.	Weight of second component.	Temp.	Pressure, mm.	Volume found.	Volume measured at N.T.P.	Theoretical value.
14	β-Naphthol + benzophenone	0·2694	0·2188	12°	744	44·9	42·1	41·6
15	β-Naphthol + ethyl benzoate	0·2318	0·1848	12	744	39·5	37·0	35·8
16	Ethyl salicylate + ethyl benzoate	0·2926	0·1694	12	736	43·3	40·2	39·2

If, however, we attempt to carry out such estimations, using phenetole as the solvent, we are at once face to face with a chemical equilibrium, such as is indicated in table I, so that there is less methane liberated than corresponds with the quantity of hydroxy-compound present in the mixture.

A series of experiments carried out in phenetole solution, using mixtures of α-naphthol with ethyl propionate, benzoate, and benzophenone respectively, gave the following values:

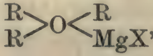
TABLE III.

Estimation of Hydroxy-compounds in Mixtures (Phenetole Solutions).

No. of expt.	Mixture.	Weight of α-naphthol.	Weight of second component.	Temp.	Pressure, mm.	Vol. found.	Vol. at N.T.P.	Theoretical value.	Vol. found × equilibrium factor (=1·08).
17	α-Naphthol + benzophenone	0·2623	0·2182	11·0°	740	40·6	38·0	40·5	41·0
18	α-Naphthol + ethyl benzoate	0·2374	0·1716	12·0	743	36·2	33·9	36·6	36·6
19	α-Naphthol + ethyl propionate	0·1873	0·1130	12·3	761	28·7	27·5	28·9	29·7
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)

As indicated in columns 8 and 9, there is a considerable divergence from the theoretical figures, but if we multiply the volume of methane obtained by the equilibrium factor for α-naphthol, which according to table I is equal to 1·08, we obtain in this way the figures quoted in column 10, such values apart from the experimental errors involved in manipulation being identical with those calculated according to theory. This result, which apparently establishes the fact that the presence of a second substance (ketone, ester, etc.) does not exert any disturbing influence on the equilibrium value of the hydroxy-compound, is an important one in view of the succeeding paper, "A method for determining the relative reactivity of organic compounds."

With regard to the specific nature of the equilibrium under discussion, namely, the one which is met with when hydroxy-compounds are treated with magnesium methyl iodide in phenetole solution, nothing definite can be said at present, but the author ventures to put forward the following tentative theory in explanation:

The constitution of the additive compounds formed from magnesium alkyl halides and ethers has been the subject of much discussion. They were first formulated by Grignard (*Compt. rend.*, 1903, **136**, 1260; *Bull. Soc. chim.*, 1903, [iii], **29**, 944) as possessing the general structure  $\begin{smallmatrix}R\\R\end{smallmatrix}\!>\!O\!<\!\begin{smallmatrix}R\\MgX\end{smallmatrix}$, whilst Baeyer and Villiger (*Ber.*, 1902, **35**, 1201) regard them as oxonium compounds of the type ${}^{R}_{R}{>}O{<}^{MgR}_{X}$. According to the later work of Tschelinzeff (*Ber.*, 1905, **38**, 3664; 1906, **39**, 773, 1674, 1682, 1686; 1907, **40**, 1487; *Compt. rend.*, 1907, **144**, 90) these derivatives possess marked similarity to the additive compounds obtained from tertiary amines and magnesium alkyl halides, namely, $NR_3(MgR)I$. Since the latter must be regarded as true ammonium salts, namely, $R_3N{<}^{MgR}_{I}$, it follows that the ether derivatives possess a similar oxonium structure, ${}^{R}_{R}{>}O{<}^{MgR}_{I}$.

In contrast with these views is the well known theory of additive compounds developed by Werner (*Annalen*, 1902, **322**, 296; "Neuere Anschauungen auf dem Gebiete der anorganischen Chemie"). This author assumes that in the formation of a so-called oxonium compound the oxygen does not function as a quadrivalent element, but in the change from an oxygen derivative to an oxonium salt only a third valency of the oxygen atom becomes operative, whilst simultaneously the acid radicle (X), instead of attaching itself to the fourth valency, is attracted and held, first, by a partial valency exerted directly through the radicle to which it was attached originally by a normal valency, and secondly, through an indirect more distant attractive force between it and the oxygen atom; thus oxonium and sulphonium salts are written $[R_2O \cdots\cdots (H)R']X$ and $[R_2S \cdots\cdots (H)R']X$, the halogen (X) in each case being attached by a direct partial valency to H or R′ respectively, and by an indirect one to the rest of the molecule through the oxygen or sulphur atom. The latter indirect attraction Hantzsch (*Ber.*, 1905, **38**, 2162) prefers to regard as being "general" rather than "specific" in character, that is, not exerted through one particular atom (O or S), but attributable to the sum total attractive force exerted collectively on the halogen by the rest of the molecule. Corresponding with this scheme the additive compounds of ethers with magnesium alkyl halides have been formulated according to the general type $[R_2O \cdots\cdots (Mg)R']X$, in which the magnesium alkyl radicle is represented as attached to the oxygen atom by a direct partial valency, the halogen being only attached indirectly.

Whether we regard the oxonium theory or Werner's as the more correct, there is no a priori reason why, depending on the nature of the radicles (R) and (R′), there should not exist compounds of both the types (1) ${}^{R}_{R}{>}O{<}^{MgR'}_{I}$ and (2) ${}^{R}_{R}{>}O{<}^{MgI}_{R'}$ [or, according to Werner, $(R_2O \cdots\cdots MgR')I$ and $(R_2O \cdots\cdots MgI)R'$]. No such structural isomerides have been obtained up to the present, but the author ventures to think that in the reaction between various hydroxy-derivatives and magnesium methyl iodide in phenetole solution, both of these types of substances may be formed, namely:

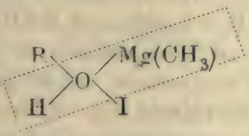
$$(3)\ \begin{matrix}\text{R}\\\text{H}\end{matrix}\!>\!\text{O}\!<\!\begin{matrix}\text{Mg}\cdot\text{CH}_3\\\text{I}\end{matrix} \quad \text{and} \quad (4)\ \begin{matrix}\text{R}\\\text{H}\end{matrix}\!>\!\text{O}\!<\!\begin{matrix}\text{MgI}\\\text{CH}_3\end{matrix},$$

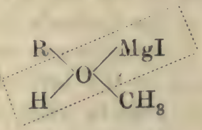
or, according to Werner:

$$\left[\begin{matrix}\text{R}\\\text{H}\end{matrix}\!>\!\text{O}\cdots\cdots\text{Mg(CH}_3)\right]\text{I} \quad \text{and} \quad \left[\begin{matrix}\text{R}\\\text{H}\end{matrix}\!>\!\text{O}\cdots\cdots\text{MgI}\right]\cdot\text{CH}_3,$$

one of which is unstable, breaking down at once into methane and Mg(OR)I, the other being relatively stable.

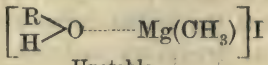
If we consider formulæ (3) and (4) it is not at first sight apparent which of these two structures represents the stable form, but the fact may be noted that in the particular groupings enclosed in the dotted figures below we have:

(3a) 

(4a) 

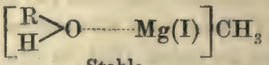
in the one case the radicle $-\text{Mg(CH}_3)$ attached to $-(\text{OH})$, and in the other case $-(\text{MgI})$ attached to the hydroxyl group. Judging from the reactive nature of the positive complex $-\text{Mg(CH}_3)$, it would seem that in such circumstances this must at once react with the negative hydroxyl group with the liberation of methane and formation of Mg(OR)I, whilst in the case of the substance denoted by the structure (4*a*) there seems to be no valid reason why such a derivative should not be stable, since it represents an additive compound of the type $\overset{+}{\text{MgI}}-+-\overset{-}{\text{O}}\!\!<\!\!\begin{matrix}\text{CH}_3\\\text{H}\\\text{R}\end{matrix}$, and the strong affinity of magnesium halides for alcohols and ethers is a well known fact. If such a theory is correct, then evidently the less negative the complex $-\overset{-}{\text{O}}\!\!<\!\!\begin{matrix}\text{CH}_3\\\text{H}\\\text{R}\end{matrix}$ becomes, the less the tendency would be towards the formation of a compound of the latter type (4*a*), a result which would evidently be brought about by increasing the positive character of the alkyl group (R) in the alcohol employed; thus in passing up the series from methyl to amyl, the tendency towards the formation of the second isomeride $\begin{matrix}\text{R}\\\text{H}\end{matrix}\!>\!\text{O}\!<\!\begin{matrix}\text{MgI}\\\text{CH}_3\end{matrix}$ should gradually diminish, until finally the positive nature of the radicle (R) becomes so pronounced that such an isomeride is no longer capable of existence. In this case only the unstable isomeride $\begin{matrix}\text{R}\\\text{H}\end{matrix}\!>\!\text{O}\!<\!\begin{matrix}\text{Mg(CH}_3)\\\text{I}\end{matrix}$ would be formed, with the necessary consequence of a theoretical yield in the volume of methane evolved.

This is, in fact, borne out by the experimental results quoted above, for, as indicated in table I, the deviations from the theoretical values in the quantity of methane evolved from methyl, ethyl, and propyl alcohols are 43, 71, and 83 per cent. respectively, whilst *iso*amyl alcohol gives a normal value, or, in other words, the isomeride, $\begin{matrix}C_5H_{11}\\H\end{matrix}\!>\!O\!<\!\begin{matrix}MgI\\CH_3\end{matrix}$, is not capable of existence. A similar explanation is, of course, true if we accept the co-ordination formulæ of Werner as being the more probable, since we are then dealing with the two isomerides:



$$\left[\begin{matrix}R\\H\end{matrix}\!>\!O\cdots\cdots Mg(CH_3)\right]I$$

and



$$\left[\begin{matrix}R\\H\end{matrix}\!>\!O\cdots\cdots Mg(I)\right]CH_3$$

Unstable. Stable.

Whilst in the above discussion we have considered the reaction simply as one between magnesium alkyl halide and R(OH), it is, of course, in reality one between the additive compound formed by the union of the solvent with the magnesium alkyl halide, and R(OH). Just in what particular the rôle of the "solvent additive compound" differs from that of the magnesium alkyl halide alone is uncertain, but it undoubtedly plays some part in the above series of changes.

It is unfortunate that Zerewitinoff has not carried out any experiments with the lower fatty alcohols in pyridine solution, but with the nearest approach to these derivatives, namely, in the case of propyl mercaptan (*Ber.*, 1908, **41**, 2237), it is a fact that the divergence from the theory in the value of the methane evolved as noted by him is much more pronounced than in the case of any of the other substances investigated.*

In a recent interesting communication by Oddo (*Ber.*, 1911, **44**, 2048) this author has modified the usual procedure of measuring the volume of gas evolved, substituting for this, by the use of a simple piece of apparatus, a direct determination of its weight. It would seem that, to quote from his paper, abnormal results were also encountered by him when solvents other than pyridine were employed, for he states (*loc. cit.*, p. 2048), "Mit den anderen Lösungsmitteln habe ich in einigen Fällen Zahlen bekommen welche kaum die Hälfte der Theorie erreichten." According to his figures, ethyl and propyl alcohols give normal values, and it is unfortunate that one cannot gather from his results just exactly the nature of the solvent used with these particular substances.

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* Since writing the above, the author is pleased to learn that, at his suggestion, further work on the estimation of the lower fatty alcohols and fatty amines in pyridine and other solvents has been undertaken by Mr. A. P. Tanberg, B.Sc., in the chemical laboratory of Swarthmore College, Swarthmore, Pennsylvania, U.S.A.

Part II.—Experiments with Amino- and Imino-derivatives.

In view of the foregoing it was decided to re-investigate the behaviour of the amines, and more especially that of the lower fatty amines towards the Grignard reagent, since apparently the latter substances have not up to the present been experimented with. The author's first estimations carried out with aromatic amines in both phenetole and amyl ether solution gave results as indicated in table IV, excess of the Grignard reagent being present in all cases.

TABLE IV.

No. of expt.	Solvent.	Substance.	Weight taken.	Temp.	Pressure, mm.	Vol. found.	Vol. at N.T.P.	Theoretical value.
20	Phenetole	Diphenylamine	0·2650	11·5°	772·0	30·7	29·9	34·9
21	,,	,,	0·2960	12·7	768·0	34·6	33·4	38·95
22	,,	*p*-Chloroaniline	0·2516	12·1	763·6	40·9	39·3	43·9
23	,,	Ethylaniline	0·2132	14·0	756·0	37·5	35·5	39·2
24	Amyl ether	,,	0·2401	13·4	768·5	45·4	43·8	44·1

Apparently we are also dealing here with an equilibrium in the phenetole solution, the factor for which with diphenylamine has a value equal to 1·17; in amyl ether solution, on the contrary, we find a normal value, due also in this instance presumably to the insolubility of the magnesium additive compound in this solvent. An attempt to estimate diphenylamine in a mixture of this with benzophenone in phenetole solution gave the following result:

Expt. 25.—0·2976 Gram of diphenylamine, mixed with 0·2182 gram of benzophenone and treated with excess of the Grignard reagent, liberated 35·9 c.c. of methane measured at 11° and 740 mm. = 33·6 c.c. at N.T.P. (theory requires 39·2 c.c.).

If we multiply the volume found (33·6) by the "equilibrium factor" for diphenylamine, which is equal to 38·95/33·4 = 1·17 (experiment 21), we have 33·6 × 1·17 = 39·3 c.c., a figure sufficiently close to the theoretical value.

It is, however, with the lower fatty amines, for example, diethylamine, dipropylamine, di*iso*butylamine, di*iso*amylamine, etc., that we encounter the most anomalous results, for an investigation of these substances showed, in the first place, that neither in phenetole nor in amyl ether solution is there any vigorous evolution of methane at the ordinary temperature when these derivatives are mixed with a solution of the Grignard reagent in one or other of these solvents; thus, for example, when di*iso*butylamine and magnesium methyl iodide are brought together at the ordinary temperature using either of the above solvents, there is no gas evolved, and, further, the decomposition takes place only partly at 50°, and is only completed after heating for some time at 100°. With regard to the remaining amines they apparently form less stable additive products than di*iso*butylamine, but also here the additive compounds decompose very slowly, so that only after keeping from four to five hours at the ordinary temperature do we have approximately the theoretical quantity of methane liberated. The decomposition in the case of benzylamine in amyl ether solution is very striking, for on mixing the solution of amine with the solution of magnesium methyl iodide in amyl ether a voluminous, white precipitate of an additive compound is immediately produced, which on shaking rapidly disappears, the disappearance being accompanied by a very brisk evolution of methane. The following are the details of the various experiments:

Expt. 26.—0·1775 Gram of benzylamine when treated in amyl ether solution with excess of the Grignard reagent gave 34·6 c.c. of methane measured at 12° and 769 mm. = 33·5 c.c. at N.T.P. (theory requires 36·9 c.c.).

Expt. 27.—0·1364 Gram of diethylamine was dissolved in 5 c.c. of amyl ether, and 5 c.c. of the Grignard solution were added. After mixing and shaking well for from three to four minutes, the volume of gas evolved was 6·0 c.c. There was a slow evolution of gas on keeping at the ordinary temperature during the next four hours, amounting altogether to 28 c.c., when the experiment was abandoned.

Total volume of gas evolved after four hours at 12·2° and 763 mm. = 34·0 c.c. (theory requires 43·2 c.c.).

Expts. 28 *and* 29.—Dipropylamine and di*iso*amylamine exhibited a similar behaviour, both substances giving off very little gas after mixing and shaking vigorously, but characterised by the same slow, continuous evolution of gas, which amounted after some three and a-half hours to about 76 per cent. of the theoretical value.

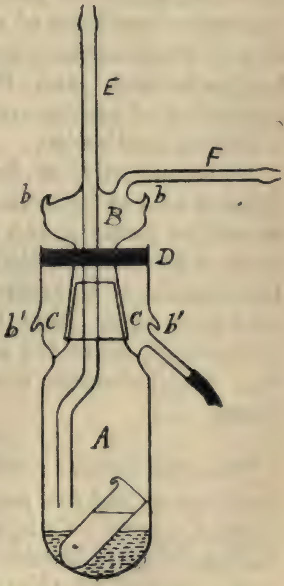
Expt. 30.—0·2230 Gram of di*iso*butylamine was dissolved in 5 c.c. of amyl ether, and 5 c.c. of the Grignard solution were added. On mixing and shaking vigorously only about 3 c.c. of gas were evolved, and there was practically no further increase on keeping for two hours at the ordinary temperature. After heating for twenty minutes at 50° the volume of gas evolved amounted to 26 c.c., and after a further twenty minutes at 100° another 13 c.c. were obtained.

Total volume of gas evolved at 13° and 763 mm. = 39·0 c.c. (theory requires 40·1 c.c.).

In phenetole the stability of these additive compounds of amine with magnesium methyl iodide is even more pronounced, as is illustrated by the following experiment carried out with di*iso*amylamine in this solvent.

Expt. 31.—0·2536 Gram of di*iso*amylamine was dissolved in 2·5 c.c. of phenetole, and mixed with 7·5 c.c. of a phenetole solution of magnesium methyl iodide. There was no gas evolved on mixing, but after shaking vigorously for four or five minutes some 3 or 4 c.c. were liberated. After remaining for twelve hours at the ordinary temperature the volume of methane evolved at 12° and 771 mm. amounted to only 14 c.c. (theory requires 36·95 c.c.).

It is important to note that the abnormal behaviour with the above amines occurs with both solvents, namely, amyl ether and phenetole, and in both cases we are dealing with magnesium additive compounds of the amines soluble in these solvents. An attempt was made to determine the reaction velocity of the above decomposition in amyl ether solution, but the absence of a suitable arrangement for stirring, whereby a supersaturated solution could be avoided, rendered it impossible to obtain constants of any value. All of the determinations noted in this paper were carried out in the manner previously described, except that a modified form of the apparatus was employed, in which by the use of a ground-glass stopper it was hoped to eliminate any changes caused by the use of rubber stoppers. The apparatus * (as shown in the accompanying sketch) consists of a cylindrical glass bottle (*A*) of about 200 c.c. capacity fitted with a ground-glass stopper (*B*), and supplied with a mercury joint (*C*). The mercury is kept in position during the shaking by means of the rubber stopper (*D*), and two rubber bands drawn over the projections (b'—b') prevent the glass stopper from working loose. The air is displaced by passing dry nitrogen through the tube (*E*), and the methane evolved measured by connecting (*F*) to a Lunge nitrometer or Hempel burette filled with dry mercury. The solutions of magnesium methyl iodide in amyl ether and phenetole were made according to the methods previously described.



General Conclusions.

(1) Most hydroxy-compounds give low values when estimated by Hibbert and Sudborough's method (Trans., 1904, **85**, 933), using phenetole as the solvent. The lower fatty alcohols, up to and including propyl alcohol, behave in this respect quite abnormally, not only in phenetole, but also in amyl ether. It is suggested that this abnormal

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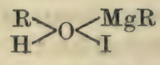
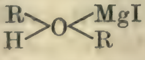
* Made by Pressler, Glasbläserei, Leipzig.

behaviour may be due to the formation of isomeric compounds of the type:



$$\begin{matrix}R\\H\end{matrix}\!>\!O\!<\!\begin{matrix}MgR\\I\end{matrix}$$

and



$$\begin{matrix}R\\H\end{matrix}\!>\!O\!<\!\begin{matrix}MgI\\R\end{matrix}$$

(but possibly also containing one or more molecules of the solvent) in solution, although no definite evidence of their existence has been obtained. It would seem that in the case of various alcohols we are dealing in solution with an equilibrium of two isomerides of the above type, only one of which is unstable enough to decompose.

(2) Aromatic hydroxy-compounds and the majority of the fatty hydroxy-derivatives may be estimated with considerable accuracy by using amyl ether as solvent, both alone and also in mixtures of them with other derivatives, such as ketones, esters, etc.

(3) The aromatic amines give low values in phenetole solution, which may likewise be due to the formation of isomeric compounds similar to those indicated above. In amyl ether normal values are obtained.

(4) The lower fatty amines form with magnesium methyl iodide, both in phenetole and amyl ether solution, additive compounds of such stability that either no decomposition occurs at the ordinary temperature, as in the case of di*iso*butylamine, or we have a slow, continuous evolution of gas extending over many hours, and which is only complete in various cases on heating. The method proposed by Sudborough and Hibbert (Trans., 1909, **95**, 477) for the estimation of amino- and imino-groups possesses accordingly only a limited application.

(5) Apparently, as Zerewitinoff found, pyridine is the most suitable solvent for estimating the majority of hydroxyl derivatives, as well as primary and secondary amines, but as no experiments have as yet been carried out with the lower fatty alcohols or the fatty amines in this solvent, nothing definite can be said at present in regard to its general application. From a few preliminary experiments, which the author was able to perform, it would appear that dimethylaniline could be substituted for pyridine with equal success.

The experimental part of this and the two succeeding investigations was carried out, partly at the Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth, and partly at the Imperial College of Science, London, during the session 1908–9. The author desires in this connexion to tender his best thanks to Professor Sudborough and Sir William Tilden for their kindness,

and the facilities they were good enough to place at his disposal. He is also indebted to the Chemical Society for a grant towards the expenses of the research.

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XLI.—*A Method for Determining the Relative Reactivity of Organic Compounds.**

By HAROLD HIBBERT.

IN the preceding communication (p. 328) it was shown that whilst in the reaction between a hydroxy-compound and magnesium methyl iodide in phenetole solution, in which all the reaction products, apart from the methane, are soluble, the total theoretical quantity of methane is not, in general, evolved (due presumably to the formation of an equilibrium between two isomeric compounds), yet in presence of other organic derivatives (ketones, esters, etc.), provided excess of magnesium methyl iodide is present, the same percentage amount of methane is always evolved from the same hydroxyl derivative. In other words, the presence of the second component, which results merely in the formation of an additive compound with no subsequent liberation of methane, does not interfere with the reaction, as between hydroxy-compound and magnesium alkyl halide. This is also clearly indicated in the series of experiments quoted in table I below, in each of which 0·2500 gram of α-naphthol was mixed with a weighed amount (1/1000 gram-molecule) of the respective ketones, the mixture dissolved in 5 c.c. of phenetole, and then caused to react with 7 c.c. of a solution of magnesium methyl iodide in the same solvent, this quantity being

TABLE I.

Mixture taken.	Weight of ketone.	Temp.	Pressure, mm.	Vol. found.	Vol. at N.T.P.	Theoretical value.	Methane evolved, per cent.
α-Naphthol + methyl ethyl ketone.........	0·0720	11°	747	37·96	35·9	38·6	93·0
α-Naphthol + methyl propyl ketone	0·0860	11	747	38·0	35·9	38·6	93·0
α-Naphthol + acetophenone	0·1201	11	747	38·5	36·4	38·6	94·3

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* The abstract of this paper appeared in Proc., 1909, 25, 57.

slightly more than sufficient to combine with both hydroxy-compound and ketone; in no experiment quoted in this paper was there a separation from the solution, apart from the methane, of any of the reaction products.

It is apparent from these experiments that the actual amount of methane evolved from the α-naphthol is independent of the presence of the ketone, for it was shown in the preceding paper (p. 331) that with α-naphthol alone in phenetole solution the amount of methane evolved in presence of excess of the Grignard reagent corresponds with the above value (93 per cent.).

If now to such a mixture of α-naphthol and ketone a quantity of the magnesium alkyl halide insufficient to combine with both hydroxy-compound and ketone is added, evidently a partition of the Grignard reagent between the two components will take place, the amount appropriated by each being dependent on the relative reactivity of each substance for the reagent in question. With the same quantity of hydroxy-compound, using equimolecular amounts of various ketones, and the same (insufficient) quantity of the phenetole solution of magnesium methyl iodide, the difference between the actual amount of methane evolved and that corresponding with the weight of hydroxy-compound taken will evidently serve as a measure of the relative reactivity of the ketone towards the Grignard reagent under the given conditions. This statement is, of course, based on two assumptions: in the first place, that the reaction between α-naphthol and magnesium methyl iodide in phenetole solution is not influenced by the presence of the ketone, and in the second place that the sum total of the various physical factors, steric hindrance, etc. (the so-called passive resistance), which may come into operation in this particular reaction is of the same order of magnitude for the various ketones. With respect to the first, the experiments quoted in table I serve, as already stated, to indicate that the character of the reaction is not affected by the presence of the ketone, and as regards the second it seems probable that with substances constituted analogously (and especially with members of a homologous series) the various physical factors which might conceivably influence the reaction velocity between the ketone and Grignard reagent are of approximately the same order of magnitude, although the recent work of Brunel (*Ber.*, 1911, **44**, 1000; *Annalen*, 1911, **384**, 245) on the equilibrium between *iso*butyl and *tert.*-butyl bromide proves that this statement is not true generally.

Acting on these assumptions the relative reactivity of a series of ketones towards magnesium methyl iodide in phenetole solution has been determined in the following manner:

0·2880 Gram of α-naphthol (1 mol.) was mixed with an amount of the ketone equivalent to three molecules, the mixture dissolved in 6·0 c.c. of phenetole, and then caused to react with 5·0 c.c. of a solution of magnesium methyl iodide in phenetole, this quantity being exactly the calculated amount necessary to react with the whole of the α-naphthol (0·2880 gram). All the experiments were carried out at the same temperature, and the volume of methane evolved measured in the usual manner by means of the apparatus described in the preceding paper. The amount of gas evolved has in all cases been calculated to N.T.P. for the purpose of comparison.

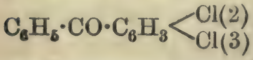
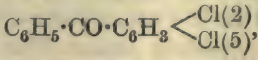
TABLE II.

Mixture.	Weight of ketone.	Temp.	Pressure, mm.	Vol. of methane found.	Vol. at N.T.P.	Theoretical value.	Reactivity factor = theor. value/exp. value.
α-Naphthol + acetone	0·3483	11°	751·0	16·5	15·7	44·5	2·8
α-Naphthol + methyl ethyl ketone..........	0·4324	11	751·0	27·1	25·75	44·5	1·7
α-Naphthol + methyl propyl ketone	0·5165	11	751·0	29·9	28·4	44·5	1·57
α-Naphthol + methyl *iso*propyl ketone ...	0·5165	11	751·0	31·6	30·0	44·5	1·48
α-Naphthol + methyl butyl ketone.........	0·6006	11	743·5	14·2	13·36	44·5	3·3
α-Naphthol + methyl *iso*butyl ketone ...	0·6006	11	741·2	19·6	18·4	44·5	2·4
α-Naphthol + phenyl methyl ketone	0·7206	11	751·0	28·4	27·0	44·5	1·65
α-Naphthol + diphenyl ketone	1·0925	11	747·4	34·3	32·4	44·5	1·4

In the last column is given the ratio of the theoretical quantity of methane corresponding with 0·2880 gram of α-naphthol to the amount actually found, and this, from the author's point of view, serves in a general way to indicate the relative reactivity of the ketones towards magnesium methyl iodide under the given conditions.

Although the results quoted above are to be considered only in the light of a preliminary investigation, no great accuracy being claimed for them, it is of interest that the well-known greater reactivity of the fatty ketones over that of the aromatic should also stand out so prominently in these experiments.

The author regrets having to abandon the above line of work owing to his entrance into the industry, for an extended investigation of the subject would naturally include esters, nitriles, amines, imines, alcohols, etc., in fact, any of the compounds on which the Grignard reagent has been used with such conspicuous success. The results of such an investigation might be expected to prove of considerable value in determining the best conditions for any given type of reaction involving the use of magnesium alkyl halides.

A further instance of the value of the principle outlined in this paper will be found, for example, in its adaptation to determine the validity of the assumption of the equality of the 1 : 3- and 1 : 5-positions in the benzene nucleus. It would only be necessary to determine the relative reactivities of two ketones, for example,  $C_6H_5{\cdot}CO{\cdot}C_6H_3{<}\begin{smallmatrix}Cl(2)\\Cl(3)\end{smallmatrix}$ and  $C_6H_5{\cdot}CO{\cdot}C_6H_3{<}\begin{smallmatrix}Cl(2)\\Cl(5)\end{smallmatrix}$, towards the Grignard reagent when mixed with the same quantity of α-naphthol by the method indicated above.

XLII.—*A New Method for the Separation of Tertiary from Secondary and Primary Amines.*

By Harold Hibbert and Archibald Wise.

In the preceding communication a method has been described for determining the relative reactivity of organic compounds towards the Grignard reagent, and it was pointed out that the method could be applied, not only to the ketones (the immediate subject under discussion), but also to a large variety of other types of organic substances; thus we should expect to find on theoretical grounds a very pronounced difference in the reactivity of primary, secondary, and tertiary amines towards the Grignard reagent, as well as in the relative stability of their respective additive compounds. In the case of the primary and secondary aromatic amines the additive compounds formed from them and magnesium alkyl halides are extremely unstable at the ordinary temperature, decomposing practically instantaneously with evolution of the corresponding fatty hydrocarbon:

$$(1)\quad R{\cdot}NH_2 + MgR'I = R{\cdot}NH(MgI) + R'H$$
$$(2)\quad R_2{:}NH + MgR'I = R_2{:}N(MgI) + R'H$$

whilst the tertiary amines, not possessing any available hydrogen atom, yield additive compounds incapable of decomposition in this manner.

If now a mixture of a secondary and tertiary aromatic amine dissolved in phenetole is treated with a phenetole solution of magnesium methyl iodide in quantity insufficient to combine with both, then evidently (assuming that all the reaction products are soluble in the solvent) a partition of the reagent between the two amines will take place, the nature of which will be indicated by the volume of methane evolved (exactly as in the case of α-naphthol and ketone quoted in the preceding paper), and which likewise should enable us to arrive at an approximate idea of the relative reactivities of the two substances toward the magnesium alkyl halide.

Determination of the Relative Reactivity of Mono- and Di-ethyl-aniline towards Magnesium Methyl Iodide in Phenetole Solution.

A mixture containing 0·3196 gram (1 molecule) of monoethyl- and 2·2155 grams (5½ molecules) of diethyl-aniline was dissolved in 5 c.c. of phenetole, and then mixed with 7·5 c.c. of a phenetole solution of magnesium methyl iodide, this quantity representing the exact theoretical amount necessary to combine with the secondary amine.

Volume of methane evolved = 52·2 c.c. at 10° and 767 mm. (theory requires 60·3 c.c.). A blank experiment with monoethylaniline alone (p. 337) showed that, due to the presence of an equilibrium in solution, only some 90·5 per cent. of the theoretical quantity of methane is evolved.

The total volume of methane corresponding with the action of the secondary amine in the above experiment is represented by $100/90{\cdot}5 \times 52{\cdot}2 = 57{\cdot}6$.

The value $60{\cdot}3 - 57{\cdot}6 = 2{\cdot}7$ c.c. therefore represents that due to the reactivity of the tertiary amine; thus in a mixture containing 5½ molecules of the tertiary to 1 molecule of the secondary amine the amount of additive compound formed by the former does not exceed 4—5 per cent. This very slight reactivity of the tertiary amine towards the Grignard reagent points at once to the probable relative unstable nature of such additive compounds, and it has in fact been found that all such derivatives from magnesium alkyl halides and tertiary amines (with the single exception of pyridine) decompose when heated to 200—280° back again into their respective components. This behaviour is in harmony with the experiments of Tschelinzeff (*Ber.*, 1907, **40**, 1495) on the heat of formation of such derivatives. This author found that with tertiary aromatic amines the amount of heat evolved was very small; for example, in the case of diethylaniline and magnesium propyl iodide amounting to only 0·78 calorie. In comparison with this behaviour the primary and secondary amines react to give still more unstable additive compounds, those of the aromatic and many of the fatty series decomposing instantly with evolution of the corresponding hydrocarbon and formation of derivatives of the type:

$$R{\cdot}NH{\cdot}MgI \quad \text{and} \quad R_2N{\cdot}MgI$$

respectively. The latter derivatives, however, are remarkably stable, and may even be heated to a dull red heat without undergoing decomposition.

Based on the above properties of the additive compounds formed from magnesium alkyl halides and the respective amines, a method has been devised for the separation of tertiary from secondary and primary amines, which, in brief, is as follows:

To the mixture of amines, either alone or dissolved in ether, is added an excess * of an ethereal solution of magnesium ethyl bromide (or methyl iodide), and the ether distilled off. The resulting product is then heated in an oil-bath to 200—280° (depending on the nature of the amine), whereupon the pure tertiary amine distils over. The bulk of the secondary or primary amine may be recovered by adding sodium hydroxide solution to the residue, and distilling in a current of steam.

Expt. 1 (separation of tri*iso*- from di*iso*-amylamine).—A mixture of 10 grams of each amine was diluted by the addition of 5—6 c.c. of dry ether, excess of an ethereal solution of magnesium ethyl bromide added, and the separation effected as above. The tertiary amine commenced to distil over when the temperature of the oil-bath was about 245°, and this was gradually increased to 280°, the last traces of amine being expelled by a current of dry hydrogen. The product on re-distillation gave 9·2 grams of tri*iso*amylamine.

Expt. 2 (separation of tri*iso*- from di*iso*-butylamine).—A mixture of 15 grams of tri*iso*butylamine with 8 grams of di*iso*butylamine was treated in the manner indicated above. 14·2 Grams of pure tri*iso*butylamine and 5·6 grams of pure di*iso*butylamine were recovered.

Other separations were successfully carried out with mixtures of: (*a*) di- and tri-ethylamine, (*b*) di- and tri-propylamine, (*c*) mono- and di-methylaniline, (*d*) mono- and di-ethylaniline, (*e*) aniline and dimethylaniline.

In the above mode of separation the tertiary amine is obtained free from all traces of primary and secondary amines, and since the former derivatives constitute trustworthy reagents for the identification of tautomeric substances (Michael, *Annalen*, 1908, **363**, 20; Michael and Hibbert, *Annalen*, 1909, **364**, 129, 64), we have here a convenient and simple means for obtaining them in the pure anhydrous condition such as is required for this work.

In conclusion, it must be pointed out that the clue to the above separation was found in the very different reactivities of the various classes of amines towards magnesium alkyl halides when determined by the method outlined in the previous paper, and it would seem to be a not altogether unreasonable supposition that an application of the method to other compounds might lead to similar valuable results.

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* It is safest to judge of this by adding the Grignard reagent until no further evolution of gas occurs.

XLIII.—*The Viscosity of Aqueous Solutions of Sodium Palmitate and the Influence of Electrolytes on the Same.*

By Frederick Denny Farrow.

It is now well established that in not too dilute aqueous solutions the alkali salts of the higher fatty acids are to be classed as electrolytic colloids, since these solutions conduct the electric current, and yet show relatively small changes of vapour pressure and boiling point. It was of interest, therefore, to examine the viscosity of such solutions and the effect of electrolytes thereon.

This question possesses also some considerable importance from a technical point of view, as will be explained in the discussion of the results obtained.

Materials.—The salt employed for these experiments was sodium palmitate. This was obtained as an anhydrous, white powder, which dissolved in hot water to produce clear solutions. It was found that these solutions were identical in viscosity with those obtained by dissolving pure palmitic acid in the calculated amount of aqueous sodium hydroxide. The simpler procedure was therefore adopted of using the anhydrous solid palmitate.

The water used in making all solutions was the laboratory distilled water. This was boiled to free it from dissolved gases, and was filtered whilst hot through cotton-wool. It was kept when necessary in well-corked, steamed-out, Jena-glass flasks.

The sodium hydroxide solution was prepared from clean metallic sodium and water. Due care was taken in its preparation and storage to exclude carbon dioxide. By titration with $N/10$-hydrochloric acid the solution was found to contain 0·687 gram-molecule of sodium hydroxide per 100 grams of solution.

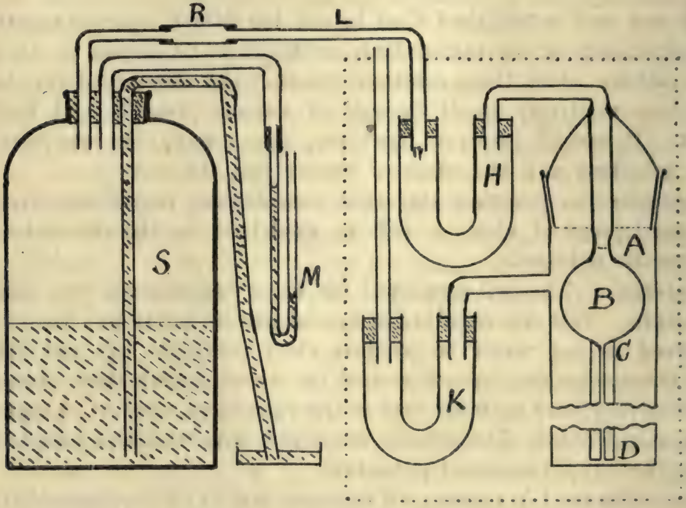
The potassium and sodium chlorides were Kahlbaum's purest, and were free from sulphates.

Methods of Measurement and Apparatus.—The viscosity measurements were made by means of an apparatus similar to one devised by Scarpa (*Gazzetta*, 1910, **40**, 271), and using a formula tested by him to calculate viscosity.

Shortly, the method consists in measuring the time, t_1, which is occupied in drawing up, through a vertical capillary tube, sufficient liquid to fill a bulb at the top of this tube, and the time, t_2, which this volume takes in flowing out from the bulb under the weight of the liquid. Given constant conditions, the viscosity of any liquid is proportional to the expression t_1t_2/t_1+t_2.

The advantage of the method lies in the fact that no density measurements are necessary, and that it is immaterial whether equal volumes of liquid are used in the different experiments. For soap solutions these advantages are very real, as the readiness with which such solutions solidify, and their tendency to form foam, makes them exceedingly difficult to measure exactly in pyknometers, or to deliver free from bubbles.

FIG. 1.



Viscometer and auxiliary apparatus.

The form of viscometer used was a modification of that used by Scarpa (*loc. cit.*). The modification consisted in substituting a ground-glass joint for the cork or rubber stopper of Scarpa's apparatus. Fig. 1 is a diagrammatic sketch (not to scale) of the viscometer and accessory apparatus.

A is a glass vessel, with side-tubes as shown, and with a glass tube sealed through its ground-in stopper. This tube is in connexion with the bulb *B*, from the bottom of which leads the capillary tube, *CD*. *H*, *K* are guard-tubes containing loosely-packed glass-wool moistened with dilute solution of sodium hydroxide. This packing serves to prevent access to the experimental solutions, of carbon dioxide, and of dust, and at the same time checks distillation from, and consequent concentration of, these solutions. *K* is open to the air on one side, and has a glass tube carried from it to above the water surface of the thermostat, whilst *H* can be joined, as shown, to the aspirator *S*. The connexion between *R* (a rubber tube) and *L* can be undone at will, *R* being then closed by a spring pinchcock. Suction is applied to *L* in order to fill the viscometer bulb after the apparatus has been charged with experimental solution.

The working of the aspirator is made sufficiently clear by the diagram. The suction exerted depends on the difference in level between the water in *S* and that in the outside dish. The measurement of this suction was effected by the water manometer, *M*, which was made to give constantly the same reading. Fine adjustment of the suction was effected by adding to, or withdrawing from, the water in the open dish.

The parts of the apparatus surrounded by a dotted line are enclosed in the thermostat. The viscometer is clamped in a holder designed to secure its accurate vertical adjustment.

Two viscometers were used, of which the essential dimensions were:

Viscometer.	Vol. of bulb.	Diam. of capillary.	Length of *C*–*D*.
A.........	8·2 c.c.	0·4 mm.	10·0 cm.
B.........	4·5 ,,	0·6 ,,	9·5 ,,

Time.—The times of flow were measured with the aid of a stopwatch, which was kept whilst in use at a constant temperature, and was used under similar conditions as to winding. Tested from time to time against a standard chronometer its rate under these conditions was found to be constant. As the measurements are all referred to a water calibration value, the question of the absolute accuracy of the time measurement does not arise.

Temperature.—For all measurements the viscometer was sunk in a gas-heated water-thermostat with glass sides. The temperature of this was maintained at $70 \pm 0{\cdot}05°$.

EXPERIMENTAL.

The experimental work divided itself naturally into two parts, namely, (1) measurements with solutions of pure sodium palmitate, and (2) measurements in which the effect of additions to these solutions was tested.

(1) *Measurements with Pure Solutions.*—The solutions were made up by exactly weighing successively the solid palmitate and the water as they were put into a small flask. The latter was then quickly heated nearly to boiling, corked, and suspended in the thermostat ready for use.

The viscometer being already clamped with its neck above the water, the required amount of the solution was drawn into a previously warmed pipette, the stopper was lifted, and the liquid delivered into the vessel. The stopper was immediately replaced in its proper position, and as quickly as possible the whole apparatus was lowered until the viscometer and guard-tubes were some 2 inches below the surface of the thermostat water. The holder was re-clamped, due care being always paid to its vertical adjustment.

The exact measurement of the volume of liquid for experiment was not required. Nevertheless, in any series of measurements the volumes used were approximately equal. The water pressure of the aspirator was kept at 20 cm. for viscometer *A*, and at 20 cm., 16 cm., and 15 cm. respectively for the different series with viscometer *B*. In any determination several readings were taken of the times of ascent and of descent. In most cases it was found that the initial readings were high, but that after the complete mixing of the liquid by a filling and emptying of the bulb the times of flow became constant. The initial high viscosity was attributed to unavoidable cooling of solutions in being transferred to the viscometer. It was certainly not attributable to any time-change of the chemical or physical nature of the solutions, as it manifested itself only in the measurements made soon after the immersion of the apparatus, and was in no way dependent on the time which had elapsed since the preparation of the solution. In view of the possibility of a gradual change of the nature of the solutions, tests were made of the viscosity from time to time over a complete day. But in no case was there any certain alteration. The following typical example shows both the initial high viscosity and the subsequent constancy over an extended time.

Viscometer A.—Concentration 0·131.

No. of reading.	Time after filling. Hours.	Mins.	t_1.	t_2.	Viscosity × 10^5.
1.	0	2	7484	9030	—
2.	0	32	7440	8812	—
3.	1	0	7390	—	—
4.	1	45	7350	8772	—
5.	3	45	7394	8746	—
6.	4	30	7372	8774	—
Mean (omitting 1) ……			7389	8776	579·8
7.	21	50	7390	8740	—
8.	22	30	7414	8770	—
9.	22	50	7356	8750	—
Mean of 7—9 …………			7386	8753	578·9
Mean of 2—9 …………			7388	8766	579·5

t_1 and t_2 respectively are the times (in 1/10th seconds) of filling and emptying the viscometer bulb. From the times the viscosity η is calculated in accordance with the formula:

$$\eta = \frac{\left(\frac{t_1 t_2}{t_1 + t_2}\right)_s}{\left(\frac{t_1 t_2}{t_1 + t_2}\right)_w} \cdot \eta_w,$$

where s and w indicate solution and water respectively.

Actually the expression $\dfrac{\eta_w}{\left(\frac{t_1 t_2}{t_1 + t_2}\right)_w}$ was obtained from measurements of the times of flow of pure water in the viscometer. The value of η_w was taken as 0·00407 in absolute units by interpolating from the data of Thorpe and Rodger (*Phil. Trans.*, 1894, **185**, *A*, ii, 397). The calibration data are as follows:

Table I.

Viscometer.	Vol. of water, c.c.	Aspirator gauge, mm.	t_1.	t_2.	$K = \frac{t_1 + t_2}{t_1 t_2}$.	$V = \frac{\eta_w}{\left(\frac{t_1 t_2}{t_1 + t_2}\right)} = K \times 0{\cdot}00407$.
A	20	200	4529	7471	3546	1443
B	20	200	431	975	3345	1361
B	20	160	930	1045	2033	8275
B	10	160	1173	847	2033	8275
B	10	150	1388	847	1911	7736

Table II.

Viscosity of Aqueous Sodium Palmitate Solutions at 70°.

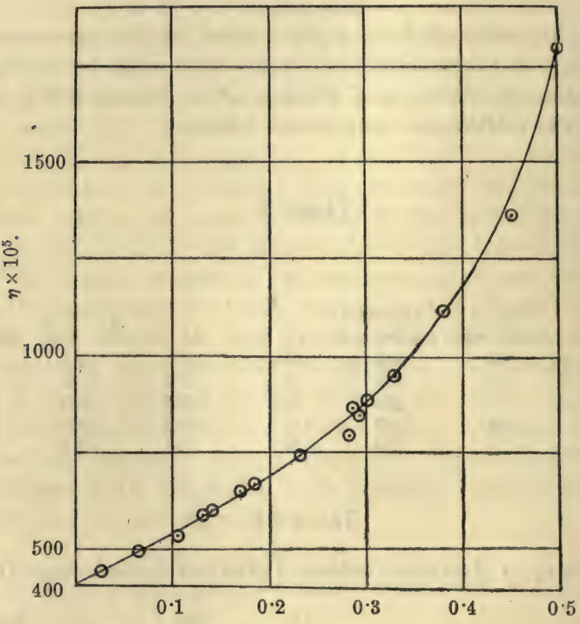
C.	t_1.	t_2.	$\frac{t_1 t_2}{t_1 + t_2}$.	Viscometer.	Constant.	Viscosity $\times 10^{-5}$.
0·026	5571	6644	3026	*A*	1443	438
0·064	6224	7394	3359	*A*	1443	485
0·105	6778	8023	3675	*A*	1443	530
0·131	7388	8766	4006	*A*	1443	579
0·141	7638	8842	4100	*A*	1443	592
0·175	8274	9780	4481	*A*	1443	647
0·187	8505	10052	4605	*A*	1443	665
0·232	9579	11125	5146	*A*	1443	743
0·283	10086	12062	5491	*A*	1443	793
0·287	11295	12813	6002	*A*	1443	866
0·293	10787	12833	5864	*A*	1443	847
0·302	11286	13470	6137	*A*	1443	886
0·329	12215	14235	6575	*A*	1443	949
0·380	14400	16658	7705	*A*	1443	1113
0·451	1437	3335	1002	*B*	1361	1363
0·499	1904	4319	1321	*B*	1361	1800

The composition (C) of table II is expressed as gram-molecules of sodium palmitate per 1000 grams of solution, and the results are shown diagrammatically in Fig. 2.

(2) *Experiments with Added Electrolytes.*—In these experiments the composition as expressed by the ratio gram-molecules of sodium palmitate/weight total water, was kept constant at the value 0·25 gram-molecule of sodium palmitate in 1000 grams of water; that is, 69·56 grams of sodium palmitate per 1000 grams of water.

The following procedure was adopted in making up the experimental solutions. Approximately the required amounts of the electrolyte solution and of pure water were weighed separately in a small flask. The total amount of water present was thus obtained, as well as the amount of salt. From the weight of water was calculated the exact amount of palmitate required. This was weighed on a piece of platinum foil, which was dropped into the flask. The latter was then rapidly heated nearly to boiling, corked, and kept in a bath of hot water until solution was accomplished. This never took longer than ten minutes. The measurements were made as with the pure solutions.

FIG. 2.



Mols. sodium palmitate per 1000 *grams of solution.*

TABLE III.

Mols. of sodium hydroxide per 100 mols. of sodium palmitate.	$\eta \times 10^5$.	Mols. of sodium hydroxide per 100 mols. of sodium palmitate.	$\eta \times 10^5$.
0·00	733	32·75	643
0·99	723	36·60	648
1·61	706	37·47	647
3·18	705	42·76	670
6·28	681	52·99	929
15·05	630	61·45	1335
20·18	621	115·32	(clear fluid too viscous to flow)
23·05	618		

TABLE IV.

Mols. of sodium hydroxide (total) per 100 mols. of palmitic acid.	$\eta \times 10^5$.
83·4	894
93·2	749

TABLE V.

Mols. of sodium chloride per 100 mols. of sodium palmitate.	$\eta \times 10^5$.	Mols. of potassium chloride per 100 mols. of sodium palmitate.	$\eta \times 10^5$.
2·01	696	1·34	694
11·18	640	12·84	622
16·42	625	25·60	600
27·97	616	50·24	723
31·39	632	64·94	1079
61·50	1767		
		Potassium and sodium chlorides.	
		24·6 NaCl	—
		21·9 KCl	—
		Total 46·5	758

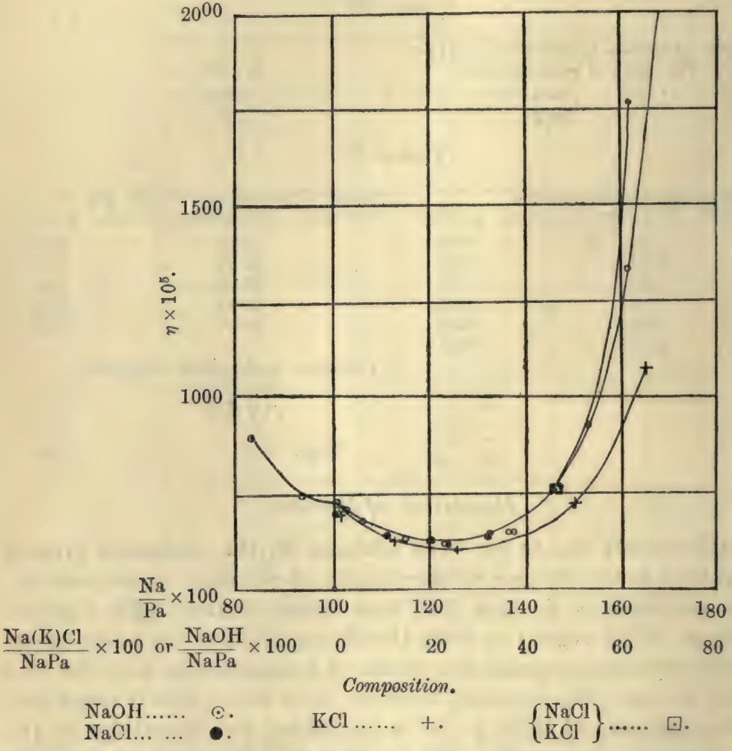
Discussion of Results.

Little success has so far been attained in the treatment from a theoretical point of view of the results of viscosity measurements. More particularly is this the case when dealing with aqueous solutions. With regard to these the attempts which have been made to find formulæ expressing the results of measurements have led to a partial success. The formulæ, however, have been entirely empirical, and as such are of little value in increasing our knowledge of the true meaning of viscosity. No attempt will therefore be made to discuss the concentration-viscosity curve, as we have no knowledge of many of the factors which are necessary for a quantitative investigation of the results obtained.

Turning to the second series of experiments it will be seen that there is an explanation required for the minima which occur on the three curves obtained. The curves for the addition of electrolyte (Fig. 3) resemble the viscosity-concentration curves of certain electrolyte solutions at low temperatures. Such solutions show a viscosity minimum at a small concentration of solute. It has been shown, however (Taylor, *Proc. Roy. Soc. Edin.*, 1905, **25**, 227), that this initial "negative viscosity" becomes less marked as the temperature is raised, and that it disappears entirely at temperatures above 30°. There can therefore be no question of the minimum observed in the present work being of the same nature as that just mentioned.

When the minimum in the present case had been established for

FIG. 3.



sodium hydroxide alone, it was considered that this could be explained by assuming an initial retardation of the hydrolysis of the sodium palmitate, with a subsequent salting-out action making itself felt on the right-hand branch of the curve. This "chemical" explanation of the initial drop in viscosity had to be abandoned when the practically coincident curve for sodium chloride was obtained. This conclusion is further justified by the precisely similar but quantitatively divergent curve for potassium chloride.

It seems probable also from other results that the behaviour of soap solutions in the way described is attributable to their functioning as colloids. Woudstra (*Zeitsch. Chem. Ind. Kolloide*, 1911, **8**, 73), working with colloidal ferric hydroxide, has found that, plotting viscosity against concentration of electrolyte, the curve shows an initial fall, with subsequent rapid rise. The smallness of the effect observed in this case is undoubtedly due to the low concentration of the colloidal substance. In the case of gelatin (Gokun, *Zeitsch. Chem. Ind. Kolloide*, 1908, **3**, 84) a similar effect has been observed, although the minimum found for measurements with freshly prepared solutions disappears if the viscosity is determined after a lapse of several hours. The complicating time effect was not observed with the soap solutions, being probably eliminated by the method of their preparation. It appears probable that the minima observed in all three cases are of the same nature, and express a general property of colloidal solutions. That soap solutions judged by the usual criteria are of this nature is well known (see Donnan and White, Trans., 1911, **94**, 1668; also footnote to the present paper). They may therefore be regarded in a certain sense as two-phase systems, in which the disperse phase is relatively concentrated, that is, contains much higher ratios of alkali and fatty acid to water than the relatively much more dilute and continuous "water phase." A portion of the water in these "colloidal particles" may be, moreover, "bound" or adsorbed. The water phase will contain a relatively small amount of the fatty-acid salt and some alkali hydroxide, the product of the hydrolysis of the soap. If, however, excess of electrolyte is present in the aqueous phase, the activity of the water in this phase is diminished, and there is a tendency for it to decrease in bulk at the expense of the water in systems in contact with it.* In the present case water may be lost by the disperse phase, with a consequent diminution of the bulk of the latter. It is this shrinkage of the colloid particles due to dehydration which is expressed by the left-hand falling branch of the curves.

There is another action of dissolved electrolytes to be considered, namely, that which results in the precipitation of suspended or colloidally-dissolved substances. That this action is exerted in soap solutions is shown by the fact that soap is "salted-out" by sodium chloride. It can well be imagined that actual precipitation is preceded by the formation in solution of aggregates; and it is suggested that the presence in the solutions, of such aggregates the size of which increases with the salt concentration, will account for the rapidly rising curve to the right of the minimum. This suggestion assumes that increasing viscosity characterises any decrease of dispersity of a colloidal solution. Woudstra (*loc. cit.*) has shown this to be the case for several inorganic colloids, and it seems reasonable to suppose that the same action is taking place in the present case. A test of this hypothesis would be to compare the ultramicroscopic appearances of palmitate solutions with different amounts of added electrolytes. This has not so far been found possible owing to experimental difficulties. It is hoped, however, soon to proceed with investigations on these lines.

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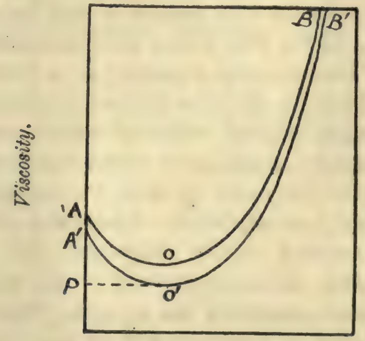
* If these systems are bounded by semipermeable membranes, and contain "more active" water, that is, more dilute solutions than the surrounding liquid, the transference is well known as the ordinary phenomenon of osmosis.

Application to Technical Practice.—Consider the curves of Fig. 4. Although the present work has determined only one such curve, it seems hardly open to doubt that for different concentrations of soap curves would be obtained approximately parallel to this. Let AOB and $A'O'B'$ be two such curves for the soap concentrations x and y. If now we start from O, the point of maximum fluidity on the upper curve, and wish to reduce the soap concentration to y, this can be done by adding the required amount of pure water. In that case the electrolyte present is also diluted, and therefore the viscosity is brought to a point on $A'O'$ some distance to the left of O'. We may even by a proper relation between the original concentration and the dilution required arrive at a point above O, the dilute solution being thus more viscous than the original. If we add not pure water, but salt solution, it will be possible so to choose the strength of this that in obtaining the soap-concentration y the electrolyte concentration is made equal to $O'P$. In this way the solution will have been diluted in the most efficient way possible if fluidity is desired. An over-concentrated salt solution will, of

FIG. 4.



Concentration of electrolyte.

course, lead to points on $O'B'$ representing rapidly increasing viscosity the more concentrated the solution added.

A case apparently analogous to that just dealt with occurs at a certain stage in the clear boiling of soap. It may become necessary to dilute the mass, which consists of sodium salts of mixed fatty acids, a certain amount of free sodium hydroxide, as well as smaller quantities of chloride and carbonate. To effect the dilution it is found necessary to add a solution of common salt of a definite concentration, which depends on the nature of the mixture present. Pure water will not mix readily with the material, whilst too concentrated brine precipitates or "cuts" the soap. Although an analogy between the two cases is obvious, it is not suggested that the technical problem can be adequately dealt with by the simple theory sketched above. The soap-boiler has complex mixtures of composition varying from day to day. He relies at present on empirical tests, the result of the tradition of the trial and error of generations. It may be, however, that viscosity measurements would serve as a further guide as to the condition of the materials in the various stages of soap manufacture.*

In conclusion, I wish to thank Professor Donnan, who suggested this work, for valuable advice, and for the interest which he has shown throughout its course.

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* When the experimental work of this paper was complete, my attention was directed to a paper by Mayer, Schaefer, and Terroine (*Compt. rend.*, 1908, **146**, 484). These authors deal with various chemical and physical properties of the sodium salts of a series of fatty acids. They state that the viscosity of soap solutions passes through a minimum in passing from acid to alkaline solution, and that the minimum lies on the alkaline side of the neutral point. The facts that no exact data of any sort are given, and that no fuller publication appears to have taken place, are held to justify the present paper. Moreover, the extension of the work to salts other than sodium hydroxide increases its scope in an important manner.

XLIV.—*The Determination of Sulphur in Petroleum.*

By JAMES MCCONNELL SANDERS.

OF the various methods proposed for determining the total sulphur in petroleum and its products, that which depends on the employment of oxygen under pressure in the Mahler or Hempel calorimetric bombs is generally conceded to be the most accurate and trustworthy. Apart from the costly and somewhat cumbersome nature of the calorimetric apparatus, and the difficulty of obtaining compressed oxygen, the method suffers from some real disadvantages in regard to rapidity of working when a number of samples have to be examined. This is more evident when the petroleum product, kerosene, for example, is poor in sulphur, necessitating several combustions in order to obtain a weighable precipitate of barium sulphate, due to the limited amount of sample which can be introduced into the bomb. In addition, the fact that for accurate results the combustion products in a gaseous state must be separately absorbed before the bomb is opened, and the liquid formed added to the total bulk of washings to be evaporated, adds a further increment of time to the total required for the operation.

The method of burning in lamps has been found by the author to give low results with some varieties of Mexican, Texan, and Canadian oils; this is due to the fact that some of the total sulphur present is in the form of an unstable compound, which is more readily decomposed during the combustion, and unless the whole of the sample taken is burnt during the determination, low results are always obtained. This method can be used, however, with some modifications described below.

Of other methods tried by the author, Goetzl's deflagration process suffers from the disadvantages inherent to such methods in general, and is, moreover, liable to result in a very impure barium sulphate precipitate from the large amount of alkali nitrates employed for the deflagration. Inner crucible methods such as that proposed by Garrett and Lomax (*J. Soc. Chem. Ind.*, 1905, **24**, 1212) requires a muffle furnace, and allows but a small amount of sample (0·7 to 1·5 grams); in the author's hands it was found to give low results for petroleum. The use of the Parr calorimetric bomb was found to give accurate and trustworthy results with heavy oils, and petroleums rich in sulphur, but the small amount of sample allowable, in conjunction with the relatively large amount of sodium peroxide, prohibits its employment for kerosenes, since the maximum charge of 0·35 gram of oil requires 10 grams of sodium peroxide and 1 gram of potassium chlorate, and in order to burn so small an amount as 1·75 grams of sample, five separate combustions would have to be made, requiring 50 grams of the peroxide and 5 of potassium chlorate, an excessive amount of salts being thus introduced into the final liquid.

In the method about to be described, the Parr calorimetric bomb is made use of, the process being arranged so as to allow of the complete combustion of 3 grams of sample in one operation, and the elimination of the inconvenient potassium chlorate from the final liquid; the process has given excellent and trustworthy results in the author's hands with all classes of petroleum, and is quite as rapid as any other practical method hitherto proposed, whilst the apparatus required is far less costly than the Mahler or Hempel bomb.

Three methods have been devised and tested by the author, and will be referred to under the headings of methods for "total sulphur" and method for "loosely combined sulphur" respectively.

Methods for Total Sulphur in Kerosenes.—(*A*) With the Parr calorimetric bomb: From 2 to 3 grams of the sample are weighed into a 100 c.c. porcelain basin, 1 centigram of finely powdered potassium bromide dusted over the surface, and 4 c.c. of pure fuming nitric acid run in from a pipette. As soon as the somewhat energetic reaction has ceased, the basin is placed on the water-bath and evaporated until the liquid changes to a dark brown colour and becomes somewhat viscous. About 0·5 gram of pure light magnesium oxide is then added, and stirred into the mass with a small steel spatula. The dish is then removed and heated over a small flame while stirring the contents thoroughly, the heating being continued until the mass shows a tendency to solidify on cooling. The amount of magnesium oxide to be used, and the extent of heating, can only be learnt by practice, but if the operation is properly performed the whole of the mixture can be removed from the dish on cooling without leaving more than a trace of oily matter. The latter is removed by adding a little more oxide, warming, and scraping with the spatula.

The granular mass thus obtained is brushed into the Parr calorimetric bomb, the standard amount of peroxide (one measure full) added, the mixture stirred with an iron rod, and after preparing the electric fuse and closing the bomb, the latter is placed in the calorimeter filled with water, and fired. A few seconds after firing the bomb should be removed from the water and the temperature allowed to rise, while rotating it between the fingers, the object being to allow the mass to fuse and burn thoroughly any large particles of carbonaceous matter. The temperature should not be allowed to rise high enough to injure the rubber washer in the base of the apparatus, the bomb being placed in the water again should it become too hot.

When the combustion is over, which usually takes about forty-five seconds, the bomb is cooled, opened, and the fused mass projected into about 25 c.c. of distilled water in a 200 c.c. nickel beaker, the washings from the bomb added, the beaker covered with a watch-glass, and as soon as the reaction between the water and the excess of peroxide has ceased, concentrated hydrochloric acid is run in, a few drops at a time, until the liquid is slightly acid. Some iron oxide and unburnt pieces of iron fuse-wire remain, and may be separated by filtering the liquid quickly through absorbent cotton-wool.

The liquid is then boiled energetically to remove chlorine, neutralised with ammonia, and then acidified with hydrochloric acid, barium chloride added while boiling, and the liquid left for some hours in a warm place; the final volume of solution should be about 150 c.c.

It will be seen that in this method a 2- or 3-gram sample is concentrated to an amount available for combustion in the Parr bomb, and that no accelerator is required, the mixture of magnesium oxide and nitrate formed in the process taking the place of the potassium chlorate usually employed for that purpose.

Perfect combustion is obtained, and the final precipitate is not liable to be contaminated, since the salts present are principally sodium, magnesium, and ammonium chlorides, with small traces of ammonium nitrate and iron.

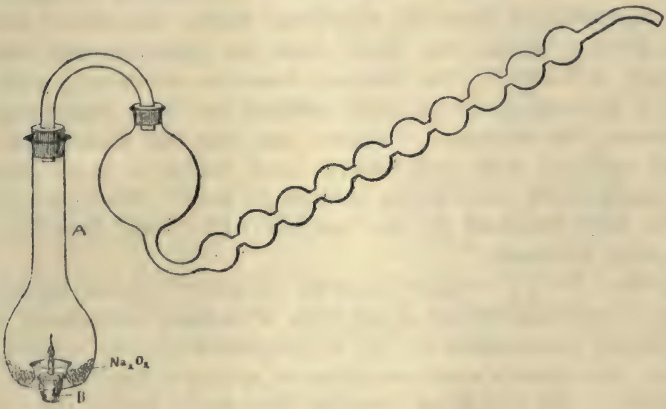
Comparative determinations made by this method and by the Mahler bomb gave the following results:

		Total sulphur, per cent.	
		Mahler bomb.	Author's method.
No. 1.	Mexican kerosene	0·80	0·80
,, 2.	,, ,, ...	0·16	0·16
,, 3.	American ,, ...	0·05	0·05
,, 4.	,, ,, ...	0·12	0·12
,, 5.	,, ,, ...	0·01	0·02
,, 6.	,, fuel oil	0·68	0·68
,, 7.	Mexican ,, ,, ...	0·29	0·30

When the amount of total sulphur is very small (less than 0·01 per cent.) the modified lamp method is likely to be more accurate, since a larger amount of sample can be burnt, but the present method is rapid enough to allow of two combustions being made in less time than that required for the lamp method.

With kerosenes the operation usually takes about thirty-five minutes to obtain the liquid ready for precipitation, but with oils rich in sulphur the preliminary reaction with the nitric acid and bromide is somewhat more violent and takes longer. When a number of samples have to be examined these may be dealt with in the preliminary stage simultaneously, the final combustion in the bomb only requiring a few minutes.

(*B*) *The Modified "Lamp Method."*—A special form of lamp chimney and lamp is required for this method; the chimney, *A*, is shown in the figure, and is readily manufactured from a Jena-glass Kjeldahl flask by softening the bottom in the blow-pipe flame and producing a re-entrant bulb by aspiration. This bulb is then heated, and the upper part broken by pushing it in with a carbon rod, and the operation so conducted that an annular space is formed in the lower part of the chimney; this space serves to hold a mixture of 6 grams of sodium peroxide with 0·5 gram of anhydrous cobalt chloride, and thus charged the chimney is supported in a vertical position and connected with a Meyer absorption apparatus by means of a wide bent tube passing through corks covered with tin foil. The free end of the absorption apparatus is connected with the filter pump after filling from three to four of the bulbs with water in which a little sodium peroxide has been dissolved.



The lamp is made by closely packing a very small platinum crucible with recently-ignited asbestos, in which a small wick of the same material has been imbedded.

This wick passes through the central perforation of a Rose's crucible lid, and is supported by a small piece of pipe-clay tubing, of such a length that when the lamp is placed in position the top of this wick support is a little above the upper rim of the annular cavity in the chimney.

From 4 to 5 grams of the sample are weighed into the lamp, the latter placed in position, and lighted, the filter-pump being operated so as to aspirate a rapid current of air through the apparatus. The peroxide–cobalt mixture serves the double purpose of supplying oxygen to the flame as moisture from the lamp combustion condenses in the chimney (this extra supply of oxygen being necessary to obviate the risk of the lamp being extinguished by the violent bubbling in the Meyer bulbs), and also of absorbing the products of combustion and hastening the combustion itself.

When nearly all the oil in the lamp has been burnt, a very small gas, or preferably spirit, flame is applied to the bottom of the lamp, so as to drive off the remaining petroleum, the lamp being then heated to low redness to volatilise or burn the traces of heavy residue, whilst the fumes which are given off are carried into the chimney by the suction of the filter-pump..

At the conclusion of the operation the chimney is allowed to cool, disconnected from the absorption bulbs, and placed entirely in a 250 c.c. beaker, the liquid from the bulbs emptied into the chimney, followed by the washings from the connecting tube and bulbs. As soon as the peroxide mixture has been decomposed by the water, the chimney is washed out into the beaker, and the liquid acidified with hydrochloric acid, boiled to expel chlorine, and precipitated with barium chloride as usual. Good comparative results were obtained by this method with both Mexican and American kerosenes.

Method for "Loosely Combined Sulphur."—Some commercial lamp oils contain sulphur in the form of unstable compounds, which are readily decomposed by rise of temperature or by contact with metals; occasionally small quantities of hydrogen sulphide are found dissolved in the oils, being probably introduced during the refining operations. A simple qualitative method for recognising the presence of these forms of sulphur has been devised by the author, and consists in "sensitising" sheets of pure copper foil by warming them for a few minutes with a 10 per cent. solution of potassium cyanide, washing quickly with water, and then with absolute alcohol.

The copper thus prepared serves as a very sensitive indicator for the presence of unstable sulphur compounds, in some cases merely leaving a small piece in contact with the oil in the cold for a few hours results in the production of a stain varying from red to black, and in the presence of much sulphur the action has been found sufficient to attack the metal and blister it.

The statement occasionally met with to the effect that distillation over metallic potassium or sodium serves as a method for estimating total sulphur contents in the petroleum, has been proved erroneous in the case of certain Mexican and Texan oils examined by the author.

In the experiments recorded below, 100 c.c. of the oil were distilled slowly over 3 grams of metallic sodium in the form of flattened wire, exposing a large surface to the oil. When only 10 c.c. remained in the distilling flask, water was added with a few drops of bromine, the flask being closed with a tube containing sodium bromate to absorb any hydrogen sulphide likely to be given off during the decomposition of the metal. When all the sodium was dissolved, more water was added, and the solution acidified with hydrochloric acid, boiled to expel bromine, and after adding the contents of the bromate tube, again boiled and precipitated with barium chloride.

The following results were obtained:

		Sulphur found, per cent.	Total sulphur, per cent.	Per cent. of total.
(1)	Mexican kerosene	0·001	0·05	2·0
(2)	,, ,, ...	0·05	0·11	45·5
(3)	,, ,, ...	0·008	0·20	4·0
(4)	American ,, ...	0·002	0·29	0·68
(5)	,, ,, ...	0·005	0·13	3·85

These results show that there is apparently no direct relation between the amount of sulphur as found by the sodium method and the total contained in the oils, and when it is considered that these unstable sulphur compounds may exist in quantity sufficient seriously to attack the inner surface of a copper lamp, their determination in the technical examination of illuminating oils seems to be a desideratum.

The method described above, although trustworthy, is somewhat lengthy and troublesome, and for technical purposes requiring the examination of a number of samples, not very convenient. The following process has been used continuously by the author with concordant results: Finely cut copper turnings are warmed with 10 per cent. potassium cyanide solution until all superficial oxide has been removed and the metal has a salmon-pink colour; the mass is quickly thrown into a glass funnel, and washed, once with air-free, distilled water, and twice with methyl alcohol. The alcohol is allowed to drain away with the funnel covered with a clock glass, and the clean turnings quickly packed into a number of 100 c.c. Erlenmeyer flasks, so as completely to fill them. Fifty c.c. of the sample to be examined are run into a flask thus prepared, the mouth stoppered with a cork carrying a long tube to serve as an air condenser. The flask is heated on the hot plate for ten minutes, then the cork and tube are removed, and the petroleum allowed to boil away until about 10 c.c. remain.

The flask is cooled, and 50 c.c. of 2 per cent. potassium cyanide introduced, the copper turnings pushed down with a glass rod into the solution, and the latter warmed, while the contents are thoroughly mixed and stirred with the rod so as to bring the solution into contact with all parts of the mass of copper. The latter is then raked out into a glass funnel plugged with cotton-wool, the solution poured over the metal, the flask washed out with hot distilled water, the washings being poured over the copper in the funnel. As a general rule the black coating of copper sulphide is easily and quickly removed by the action of the cyanide solution, in spite of the oily residue of petroleum which remains in the flask. If, however, a difficulty is experienced in removing the black stain, it is better to wash out the flask and copper turnings with absolute alcohol, pouring the alcoholic solution over the cotton-wool in the funnel in order to retain any small detached particles of copper sulphide. After washing the wool once more with alcohol and then with water, and rejecting the washings, the treatment with the cyanide solution may be proceeded with as described, using the same filter to receive the cyanide washings. The sulphur originally present in the petroleum in the unstable form or as hydrogen sulphide is now found in the form of copper sulphide dissolved in potassium cyanide. It may be estimated gravimetrically by adding concentrated bromine water, then hydrochloric acid, and boiling for some time, preparatory to precipitation with barium chloride, or volumetrically by titrating with ammoniacal silver nitrate, until a portion of the filtered liquid begins to show a faint turbidity on acidifying with hydrochloric acid.

In the manipulation of the small precipitates obtained in the gravimetric estimation of sulphur in petroleums, the author has found the following to be a convenient method of procedure. A platinum filter disk is cut from stout foil about 12 mm. in diameter, and perforated closely by means of a needle.

This disk fits loosely into a small, flat platinum dish about 5 mm. deep, the disk and dish together weighing about 4 grams. After igniting the two and weighing, the disk is placed in a funnel, the stem of which passes through a rubber stopper in the upper orifice of a tubulated bell-jar standing on a ground-glass plate. Small circles of thick filter-paper are cut a very little larger than the platinum disk, and two are placed in position over the latter, moistened with water, and sucked into contact by connecting the filter-pump with the bell-jar. A beaker is placed under the funnel to receive the filtrate, and the solution to be filtered is decanted rapidly on to the double filter paper, the precipitate being finally transferred in such a manner that it falls as nearly as possible in the centre of the paper. After washing, it will be found that the precipitate tends to creep up the walls of the funnel, and this is overcome by washing down two or three times with absolute alcohol, which also serves to dry the precipitate. The air pressure from the pump is then removed, and the paper and precipitate carefully lifted with forceps and placed in the platinum dish, the disk being on the top. Any traces of precipitate remaining in the funnel are removed with a minute swab of absorbent cotton, which is also placed beneath the disk in the dish. The latter is immediately ignited, and after the alcohol flame and that due to the paper has become extinguished, the dish is heated to redness, cooled in the desiccator, and weighed. The disk is then held over the dish with the forceps, tapped gently to dislodge any adhering precipitate, and used to collect a further precipitate or precipitates, only one weighing being thus necessary for the second and subsequent operations. When many samples have to be examined the author has found it convenient to use a train of three-necked Woulfe bottles, each provided with light tap-funnels, for the filtration of a number of precipitates simultaneously. When the precipitate of barium sulphate is very small, the danger of losing sulphur by reduction to sulphide may be obviated by making the final washing with a solution of ammonium nitrate in alcohol.

When the density of the petroleum sample is known at the temperature of the operating room, it is convenient to measure instead of weigh the amount required, in which case the sulphur percentage may be calculated by the following formula if 3 c.c. are taken for the analysis:

$$S=\frac{P\times 45{\cdot}76}{D\times 10},$$

where S = the percentage of sulphur sought, P = the weight of barium sulphate found, and D = the density of the sample.

When 50 c.c. are taken for the estimation of the sulphur in the unstable form, the formula becomes:

$$S=\frac{P\times 27{\cdot}46}{D\times 100}.$$

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XLV.—*The Absorption of the Halogens by Dry Slaked Lime.*

By WILLIAM ARTHUR REGINALD WILKS.

ALTHOUGH the action of chlorine on slaked lime has been investigated so thoroughly, the action of bromine appears to have attracted but little notice. Berzelius (*Jahresber.*, 1832, **11**, 130) first observed that bromine reacted with slaked lime with formation of a reddish-brown product, now often called "bromine bleaching powder." If the constitution of this compound is assumed to be analogous to that of bleaching powder, it seems difficult to account for its peculiar colour. It is well known that many adsorption compounds, as in the case of iodide of starch, have remarkable colours, and it was suspected that the colour of bromine bleaching powder could be explained in a similar way. The results of experiments to be described later appear strongly to favour this supposition. When a solution of bromine in carbon tetrachloride is allowed to remain in contact with dry slaked lime until equilibrium is attained, the concentrations of the bromine in the lime and in the solution are connected by the well known exponential adsorption formula. Similar experiments were afterwards carried out with iodine and chlorine in order to compare their action with that of bromine.

EXPERIMENTAL.

Preliminary experiments showed that bromine was not absorbed by pure quicklime. The slaked lime used in the experiments was freshly prepared from pure quicklime, and dried, sometimes in a vacuum desiccator, sometimes at 110°.

When bromine dissolved in carbon tetrachloride is brought into contact with dry slaked lime, the latter gradually absorbs bromine and deepens in colour to a brick-red, the action being facilitated by frequent shaking. Equilibrium is reached in the course of a few hours, although a further very slight absorption of bromine is noticed for a much longer period. Such a slight absorption after the first equilibrium has been attained was observed by Davis in the absorption of iodine by charcoal (Trans., 1907, **91**, 1666), and he explains these results by assuming that adsorption takes place at the surface of the solid with a high velocity, after which there is a slow diffusion into the interior of the solid with the production of a solid solution. A similar explanation will be adopted here.

In the following experiment a series of stoppered bottles, each containing 1 gram of slaked lime and 100 c.c. of bromine solution, were allowed to remain, with frequent shaking, at the ordinary temperature. At the end of one hour the solution in the first bottle was analysed, and at known intervals successive bottles of the series were examined, the last bottle remaining for five days. The concentration of the solution is expressed by the number of c.c. of thiosulphate solution equivalent to the iodine value of 10 c.c. of the bromine solution.

Time.	Concentration of solution.	Time.	Concentration ot solution.
1 hour	46·6	5 hours	46·3
2 hours	46·5	6 ,,	46·3
3 ,,	46·4	26 ,,	46·2
4 ,,	46·5	5 days	45·5

The first equilibrium, therefore, is reached even at the end of one hour, whilst a further very slight absorption of bromine is observed after an interval of five days.

The effect of temperature on the absorption of bromine was found to be very slight, as can be seen by the following figures, which refer to two analogous experiments carried out at 0° and 16°:

Concentration of solution. at 16°	Concentration of solution. at 0°
46·8	46·4

There is therefore a slightly greater absorption of bromine at 0° than at 16°, but the effect of temperature is so small that it was evidently unnecessary to use a thermostat in the remaining experiments, which were consequently carried out at room temperature.

The experiments were conducted as follows: One gram of finely powdered slaked lime was weighed into a dry glass bottle fitted with a well ground-glass stopper, and 100 c.c. of a carbon tetrachloride solution of dry bromine (the solution being of known strength) were added. The carbon tetrachloride was previously dried over calcium chloride and distilled. A series of similar bottles was prepared, using the same amount of lime and bromine solution in each bottle, but varying the concentration of the bromine. The bottles were shaken frequently, and the concentration of the solutions determined at the end of twenty-four to forty-eight hours by filtering quickly through glass wool into a burette, running off 10 c.c. into potassium iodide solution, and titrating the liberated iodine with standard thiosulphate solution. The concentration of bromine in the lime was calculated from the strengths of the bromine solution originally taken and that after contact with the lime. The concentration of bromine in the solution is expressed by the number of c.c. of thiosulphate required for 10 c.c. of solution, whilst the concentration of bromine in the lime is given by the amount of thiosulphate equivalent to the bromine in 1 gram of lime. The results are calculated, unless otherwise stated, in terms of thiosulphate of such a strength that 10 c.c. of iodine solution (1 c.c. $= 0{\cdot}01282$ I) $= 37{\cdot}4$ c.c. of thiosulphate solution.

The first experiment gave the following results:

Concentration of bromine in solution.	Concentration of bromine in lime.
11·4	114·7
33·95	119·0
56·7	120·4
79·9	118·5
102·5	121·0

The concentration of bromine in the lime remained practically constant, whilst its concentration in the solution varied within wide limits. The most probable explanation of this fact would be that a chemical compound is formed, the amount of bromine added in the first bottle being more than sufficient to react with the whole of the lime. The molecular ratio of bromine to lime in the compound would be:

$$\mathrm{Br} : \mathrm{Ca(OH)_2} = 1 : 4{\cdot}4.$$

In order to study the absorption of bromine before this constant composition is reached, a second series of experiments was made with a fresh specimen of slaked lime and much weaker solutions of bromine, when the following results were obtained:

[*] Concentration of bromine in solution $= C_2$.	Concentration of bromine in lime $= C_1$.	$C_1/C_2^{\frac{1}{3}}$.
3·82	30·7	19·6
9·45	36·3	17·2
13·73	49·2	19·6
22·06	55·1	19·7
38·4	39·7	—

In this case the concentration of bromine in lime increases with the concentration in the solution, except in the last bottle of the series. The third column gives the numbers calculated from the expression C_1/C_2^n, in which the value of $n = \frac{1}{3}$. These numbers are sensibly constant, and this constancy may be explained either by assuming that bromine is in solid solution in the lime, or that it forms an adsorption compound. Here the first assumption is untenable, as in that case bromine would be dissolved in the lime in fractions of an atom (provided that bromine dissolves in carbon tetrachloride as Br_2—a most probable assumption, since iodine dissolves in the same solvent as I_2). It is concluded, therefore, that bromine and dry slaked lime form an adsorption compound.

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[*] This table has already been given in a preliminary communication (*Proc. Camb. Phil. Soc.*, 1910, **15**, 527), except that the numbers have been recalculated so as to be given in terms of the thiosulphate solution taken as the standard throughout this paper. The succeeding table appeared also in the above publication.

In this series of determinations it will be noticed that after the concentration of bromine in the lime has reached the value 55·1, there is a sudden fall to 39·7 on further increasing the concentration of the solution. Later it will be seen that the amount of bromine adsorbed by lime reaches a maximum independent of the concentration of the solution (after this has reached a certain minimum value). Such maxima of adsorption have been observed also by Schmidt in his experiments on the adsorption of acetic acid by charcoal (*Zeitsch. physikal. Chem.*, 1910, **74**, 689). It is suggested that in the last experiment the figure 39·7 represents the maximum adsorption of bromine in lime, whilst the high value of the preceding concentration, 55·1, depends on a phenomenon akin to supersolubility, and may be termed "superadsorption." Even when the bromine is in the superadsorbed condition its concentrations in the solution and the lime obey the exponential formula $C_1/C_2^{\frac{1}{3}}=k$.

In both the preceding series specimens of lime were used which had been dried for two days in a vacuum desiccator. In the following series it was dried for four weeks.

Concentration of bromine in lime.	Concentration of bromine in solution.
2·5	22·7
6·85	26·4
11·7	35·4
15·65	33·3
25·35	31·3
34·85	34·2
44·0	34·6
53·6	33·5

When the concentration of the solution is very small, the bromine is adsorbed by the lime, as in the last series of experiments, but the amount adsorbed soon reaches a maximum independent of the further increase of concentration of the solution. At first sight it might be supposed that a chemical compound is formed, but a little consideration shows that if this were the case the concentration of the solution should remain constant, while the concentration of bromine in the lime should increase gradually and then remain constant when all the lime had been converted into the compound, after which the concentration in the solution could increase. Hence the above results really show that dry slaked lime adsorbs bromine, but that a limit is soon reached when the adsorption is a maximum;

thus in the first series of experiments, where this maximum was reached in the first bottle, an erroneous conclusion was drawn (namely, that the constancy of concentration of bromine in the lime was due to the formation of a chemical compound) simply because there was then no evidence of previous adsorption.

It is stated (*Ann. Reports*, 1910, **7**, 48) that Killby has shown that "bromine bleaching powder" contains bromine in three forms, namely, as bromide, hypobromite, and as bromine more loosely combined, most probably as perbromide, to which the compound owes its colour. The conditions under which the compound was formed are not stated, so that it is impossible to compare these results with those obtained by the author. In the author's opinion the experiments recorded above show that the colour of "bromine bleaching powder" is due, not to a chemical, but to an "adsorption" compound. With lime not specially dried bromine gives also bromide and hypobromite, and if the red product formed in the above experiments is shaken with a small quantity of water the colour quickly disappears, and a mixture of calcium bromide, hypobromite, and unchanged lime remains.

The molecular ratio of lime to bromine when the adsorption reaches a maximum is, in the last series of experiments, $Ca(OH)_2 : Br = 14{\cdot}9 : 1$. Here the lime had been dried for four weeks in a vacuum desiccator, whilst in the first series, when the lime was dried for two days only, the ratio was $Ca(OH)_2 : Br = 4{\cdot}4 : 1$, so that the composition of the product at maximum adsorption is greatly altered by traces of water.

The colour of the lime deepened from yellowish-red to dark brick-red as the concentration of bromine in it increased, until the maximum of adsorption was reached, when no further change in colour was observed.

Lunge and Schoch (*Ber.*, 1882, **15**, 1883) showed that iodine reacted with slaked lime suspended in water with the production of calcium hypoiodite and iodide. Under the conditions used in the following experiments, which were carried out as previously described for bromine, this reaction did not occur, but iodine was absorbed by the lime with the formation of a dark violet product, the colour of which deepened as more iodine was taken up, until it became almost black.

Preliminary experiments, carried out like those with bromine, were made to show the influence of time on the absorption of iodine:

Time.	Concentration of solution.
1 hour	31·6
2 hours	31·5
3 ,,	31·5
4 ,,	31·4
5 days	31·1

The equilibrium is reached very quickly, but, as in the case of bromine, a further slight absorption due to diffusion into the lime can be detected.

The influence of temperature, as shown by the following figures, is seen to be very small:

Temperature	0°	17°
Concentration of solution......	29·3	29·1

The remaining experiments, therefore, were carried out at room temperature.

The first series was made with the same specimen of lime used in the last experiment with bromine. The following results were obtained:

Concentration of iodine in solution = C_2.	Concentration of iodine in lime = C_1.	$C_1/C_2^{\frac{1}{3}}$.
2·6	9·8	7·12
6·4	13·65	7·35
10·0	15·9	7·38
14·7	17·7	7·23
23·95	17·2	—
33·1	17·0	—

The phenomena observed in the case of bromine and lime reappear. The iodine concentration in the lime at first increases with the concentration in the solution, and these two concentrations are connected by the formula $C_1/C_2^n = k$, where n is one-third, as in the case of bromine. The iodine concentration in the lime reaches a maximum independent of further increase of concentration of the solution. There is to be noticed also a very slight "superadsorption."

The molecular ratio of lime to iodine at the maximum concentration is $Ca(OH)_2 : I = 29·1 : 1$, which is much less than the corresponding ratio $Ca(OH)_2 : Br = 14·9 : 1$ for the same specimen of lime.

Another series of experiments with a specimen of lime dried for two weeks in a vacuum gave the following results:

Concentration of iodine in solution = C_2.	Concentration of iodine in lime = C_1.	$C_1/C_2^{\frac{1}{3}}$.
1·5	10·1	8·81
3·05	19·86	13·76
5·24	22·9	13·20
7·43	26·3	13·50
12·04	30·5	13·32
16·65	34·0	13·33
21·26	37·5	13·53

With the exception of the first determination, the ratio $C_1/C_2^{\frac{1}{3}}$ is here remarkably constant.

Experiments were then made with dry chlorine and dry slaked lime under conditions similar to the former. Preliminary trials showed that from weak solutions of chlorine in carbon tetrachloride the whole of the chlorine was absorbed by the lime without any indication of adsorption phenomena. At first it was suspected that, as carbon tetrachloride contained carbon disulphide, the chlorine had been used in reacting with the latter according to the equation:

$$CS_2 + 3Cl_2 = CCl_4 + S_2Cl_2.$$

This reaction is stated to take place when dry chlorine and carbon disulphide are used. In these experiments, however, it was found that this reaction did not occur appreciably in three days, since a solution of chlorine in the impure carbon tetrachloride had the same iodine value at the beginning and at the end of this period. Moreover, the experiments were repeated with tetrachloride free from disulphide and with exactly the same results.

In the following series of experiments the slaked lime was dried for four weeks. The concentrations of chlorine are expressed in terms of the standard thiosulphate solution as with bromine and iodine.

Concentration of chlorine in the solution.	Concentration of chlorine in lime.
0·0	205·1
0·0	410·2
0·0	615·3
32·7	725·5
136·6	733·6
204·3	729·4

A phenomenon entirely different from that noticed in the case of bromine and iodine is observed. The concentration of the solution now remains constant (zero), whilst the concentration of chlorine in the lime increases until the latter concentration reaches a maximum, when the concentration of the solution can now increase without affecting the concentration in the lime. This points undoubtedly to the formation of a chemical compound, in which the atomic ratio Ca : Cl = 1 : 1·46.

Finally, the action of the three halogens on the same specimen of lime, which in this case was dried at 110°, was compared. The results were as follows:

Chlorine.

Concentration of chlorine in solution.	Concentration of chlorine in lime.
0·0	61·75
0·0	123·5
2·1	235·8
8·25	288·0
21·4	280·0
33·0	288·0

[25 c.c. I (1 c.c. = 0·01222 I) = 45·15 of thiosulphate solution] neglecting the third result of this series the atomic ratio Ca : Cl = 1 : 1·13.

Bromine.

Concentration in solution = C_2.	Concentration in lime = C_1.	$C_1/C_2^{\frac{1}{3}}$.
0·32	15·35	22·5
2·08	16·0	12·6
5·2	22·14	12·8
8·55	26·26	12·8
16·34	22·0	—

The molecular ratio at the maximum of adsorption is $Ca(OH)_2$: Br = 20·5 : 1. A small "superadsorption" is again observed.

The molecular ratio of lime to chlorine at the maximum of adsorption, in the specimen of lime dried for four weeks in a vacuum, was $Ca(OH)_2$: Cl = 1 : 1·46, whereas in the above specimen, dried at 110°, the ratio is 1 : 1·13. The corresponding numbers for bromine are 14·9 : 1 and 20·5 : 1; thus, whilst small differences in the dryness of the lime have comparatively little effect on the absorption of chlorine, the effect on the absorption of bromine is seen to be very great.

Iodine.

Concentration in solution = C_2.	Concentration in lime = C_1.	$C_1/C_2^{\frac{1}{3}}$.
0·202	1·55	2·64
0·464	2·51	3·25
1·10	3·30	3·20
1·76	3·85	3·19
3·10	4·80	3·19

Conclusions.

(1) When bromine dissolved in carbon tetrachloride is added to dry slaked lime, the latter adsorbs bromine until a maximum of adsorption is attained. In some cases a slight "superadsorption" is noticed. The colour of bromine bleaching powder is due to this adsorption product.

(2) The concentrations of bromine in solution (C_2) and in lime (C_1) before the maximum of adsorption is reached are connected by the equation $C_1/C_2^{\frac{1}{3}} = k$.

(3) The amount of bromine adsorbed by slaked lime depends on the dryness of the lime.

(4) Similar results were observed in the case of iodine and lime. The value n in the formula $C_1/C_2^n = k$ is one-third, as with bromine, but the constant k is different for bromine and iodine.

(5) For the same specimen of lime the molecular ratio of iodine

to lime at the maximum of adsorption is less than the corresponding ratio for bromine.

(6) Chlorine behaves quite differently from the other two halogens under the same conditions. Adsorption phenomena could not be detected, but the results indicate the formation of a chemical compound.

(7) Slight differences in the dryness of the lime have much greater effect on the absorption of bromine and iodine than on that of chlorine.

In conclusion, I wish to thank Dr. Fenton for suggesting this research, and for his interest and advice throughout.

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XLVI.—*The Methyl, Ethyl, and* iso*Butyl Esters of Di-trichloroacetyltartaric Acid, and the Existence of Minima in their Temperature-rotation Curves.*

By Thomas Stewart Patterson and Alfred Davidson, B.Sc.

Some fourteen years ago one of us, at the suggestion of Professor Percy Frankland, prepared a number of chloroacetyl derivatives of methyl and ethyl tartrate and methyl and ethyl glycerate. The first of these experiments in the case of the tartrates was made with the ethyl ester and trichloroacetyl chloride, when it was found that ethyl tartrate seemed only to react with one molecule of this chloride. Methyl tartrate, which was next examined, was also found to yield, after boiling for two days with a large excess of trichloroacetyl chloride, only a monoacyl derivative, whilst with dichloroacetyl chloride and monochloroacetyl chloride, diacyl esters were obtained (Trans., 1898, **73**, 185).

As there seemed to be involved here an interesting case of steric hindrance, it appeared to the present authors to be worth while to attempt to bring about the combination between trichloroacetyl chloride and methyl tartrate in pyridine solution, which, as is well known, often facilitates such reactions—in order to obtain the diacyl ester.

After several trials the following process gave a satisfactory result. Methyl tartrate (10 grams) was dissolved in chloroform (100 grams), and pyridine (18 grams) added. Trichloroacetyl chloride (40 grams) was then added slowly to the mixture, which was cooled in ice and salt and constantly shaken. After the addition of the chloride the mixture was left in ice for an hour, then poured into cold water, and well shaken with fresh quantities of cold water. The chloroform solution was then separated, filtered, dried over calcium chloride, and evaporated in a vacuum desiccator. About 22 grams of colourless crystals were obtained, melting at 140°. After recrystallisation from chloroform, 15 grams of a product melting at 143° were collected. (Found, Cl = 44·9, 45·7. $C_{10}H_8O_8Cl_6$ requires Cl = 45·41 per cent.) The substance was found to distil—almost to sublime—under diminished pressure. It boiled at 220°/20 mm. (oil-bath 280°). It has an odour something like that of camphor, is sparingly soluble in alcohol or ether, moderately so in chloroform, benzene, ethyl acetate, or nitrobenzene, but from most of these liquids it does not crystallise well. On remaining for some time in contact with hot alcohol or ether, for instance, decomposition readily takes place, and no crystalline product is obtained unless the solvent is evaporated off rapidly under diminished pressure. It is more readily soluble in pyridine than in any other liquid that we tried, but in this solvent it decomposed slowly at the ordinary temperature and rapidly on heating.

Owing to the high melting point of the substance we could not examine its rotation in the homogeneous condition, but for the rotation in benzene we found for $c = 4$ and $l = 2$ dcm., α_D^{17} −0·403°, whence $[\alpha]_D^{17}$ −5·04° and $[M]_D^{17}$ −23·6°. For the rotation in nitrobenzene the following numbers were obtained:

Methyl Di-trichloroacetyltartrate in Nitrobenzene. [M = 469.]

$p = 4·9$:

t	14°	20°	41·5°	70·5°	90·2°
d *	1·2783	1·2724	1·2507	1·2214	1·2016
$\alpha_D^{t°}$	−0·214°	*−0·207°*	−0·169°	−0·066°	−0·002°
$[\alpha]_D^{t°}$............	−3·41°	*−3·3°*	−2·75°	−1·10°	−0·03°
$[M]_D^{t°}$	−16·0°	*−15·2°*	−12·92°	−5·17°	−0·27°

* In the tables of this paper, the density values are interpolated from a curve drawn from the experimental points. It is then unnecessary to give the actual numbers. All interpolated data other than density values are printed in italics.

That racemisation had not occurred in the preparation of the ester was shown as follows: A small quantity of methyl di-trichloroacetyltartrate was boiled under a reflux condenser for two hours with four molecular proportions of aqueous alcoholic potassium hydroxide. The solution was then evaporated to dryness, and the residue extracted several times with ether in order to remove potassium trichloroacetate. The insoluble potassium tartrate was placed in a small distilling flask with about 20 c.c. of *iso*butyl alcohol, and dry hydrogen chloride passed during four or five hours into the solution heated on the water-bath. The excess of *iso*butyl alcohol was then distilled off as far as possible. The oily residue, which solidified on cooling, was shaken with water, collected, and dried. It then melted at 68°. After recrystallisation from light petroleum it melted at 70—71°, and on distillation under diminished pressure yielded 0·45 gram of a product melting at 72°. Of this specimen 0·302 gram, made up to 15 c.c. with nitrobenzene, gave, in a 2-dcm. tube, $\alpha_{D}^{15\cdot2} + 2\cdot28°$. Pure *iso*butyl *d*-tartrate melts at 72—73°, and gave, in a 2-dcm. tube at the same concentration, $\alpha_{D}^{16\cdot3} + 2\cdot32°$, whence $[\alpha]_{D}^{16\cdot3} + 57\cdot6°$; $[M]_{D}^{16\cdot3} + 151°$. It is clear from these figures that racemisation had not occurred in the acylation by the pyridine method.

Methyl Mono-trichloroacetyltartrate.—As we wished to compare the rotation of our di-trichloroacetyl derivative with that of the mono-trichloroacetyl ester under similar conditions, we attempted to prepare a specimen of the latter substance by the method originally used, namely, by boiling methyl tartrate with a considerable excess of trichloroacetyl chloride. To our surprise, however, we obtained, by six hours' heating, a product melting, after quick crystallisation from ether, at 143°, evidently the diacyl derivative. It appeared, therefore, that the diacyl ester can, after all, be obtained without the use of pyridine, and that the original preparation of the monoacyl derivative must have been the result of some curious chance; indeed, we found it somewhat difficult to obtain a pure specimen of the monoacyl ester. We succeeded, however, as follows: Methyl tartrate (66 grams) was dissolved in about 200 c.c. of chloroform, and 50 grams of trichloroacetyl chloride, dissolved in its own volume of chloroform, were added gradually. The mixture was then heated slowly on the water-bath to its boiling point, and kept at that temperature for about ten hours. The chloroform was then removed, and the residue distilled under diminished pressure. Two main fractions were obtained, that boiling between 100° and 163°/15 mm. being chiefly methyl tartrate, and that boiling from 163° to 190° being mainly the monoacyl ester. Each fraction was shaken with water to dissolve methyl tartrate. The oily residue was shaken with fresh water, and soon solidified. The substance was crystallised twice from xylene, when it melted at 81°, the temperature formerly quoted being 79—80°. The rotation of this sample was then determined with these results:

Methyl Mono-trichloroacetyltartrate in Nitrobenzene. [M = 323·5.]

$p = 4·75$:

t	17°	20°	20·8°	22°	48·7°
d	1·2165	1·2136	1·2130	1·2115	1·1860
$\alpha_D^{t^\circ}$	+0·462°	*0·451°*	0·445°	0·444°	0·400°
$[\alpha]_D^{t^\circ}$	+8·00°	*7·83°*	7·72°	7·71°	7·10°
$[M]_D^{t^\circ}$	+25·9°	*25·3°*	25·0°	24·9°	23·0°

For purposes of comparison we also examined the rotation of methyl tartrate (m. p. 61·5°) at a similar concentration in nitrobenzene solution.

Methyl Tartrate in Nitrobenzene.

$p = 4·94$:

t	14°	20°	27·3°	41°.
d	1·214	1·2080	1·201	1·187
$\alpha_D^{t^\circ}$	+1·25°	*1·228°*	1·212°	1·15°
$[\alpha]_D^{t^\circ}$	+20·8°	*20·5°*	20·4°	19·6°
$[M]_D^{t^\circ}$	+36·3°	*36·5°*	36·2°	34·8°

From these and the previous data we obtain the following table:

Rotation of Esters in Nitrobenzene Solution. [p = ca. 5.]

	$[\alpha]_D^{20}$.	Δ.	$[M]_D^{20}$.	Δ.
Methyl tartrate	+20·5°	12·67°	+36·5°	11·2°
Methyl mono-trichloroacetyltartrate	+7·83°	11·13°	+25·3°	40·5°
Methyl di-trichloroacetyltartrate	−3·3°		−15·2	

The introduction of one and then a second trichloroacetyl group into methyl tartrate produces about equal decrements of specific rotation, but if molecular rotation be considered, the alteration of rotation brought about by the introduction of the second acyl group is much the greater. It may be noticed also, that, whereas solution in nitrobenzene at the above concentration raises the rotation of methyl tartrate from $[M]_D^{20}$ +3·68°, the value in the homogeneous condition, to $[M]_D^{20}$ +36·5°, the rotation of mono-trichloroacetyltartrate is slightly depressed, by the same solvent, from $[M]_D^{20}$ +27·01° to $[M]_D^{20}$ +25·3°, and from analogy to the ethyl esters presently to be considered, it is practically certain that nitrobenzene has a still greater depressing effect on the rotation of the di-trichloroacetyl compound. Again, whilst nitrobenzene at 20° raises the rotation of methyl tartrate, as has just been stated, by 32·82°, the rotation of ethyl tartrate is raised by the same solvent under the same conditions from $[M]_D^{20}$ +15·78° to $[M]_D^{20}$ +71·9° (Trans., 1908, **93**, 1856), or by more than 56°.

Ethyl Di-trichloroacetyltartrate.—We attempted also to prepare the di-trichloroacetyl derivative of ethyl tartrate by the pyridine method, but were unable to isolate a definite compound. A viscid residue was obtained, which gave a positive rotation, gradually changing into a negative one. However, on boiling 40 grams of ethyl tartrate with 100 grams of trichloroacetyl chloride for twenty-four hours, and, after removal of the chloride, fractionating the residue under diminished pressure, a product was obtained having $\alpha_D^{17\cdot5} + 20\cdot308°$. This was divided by distillation into two fractions, of which the first, boiling at 205—208°/14 mm., had $\alpha_D^{19\cdot4} + 20\cdot826°$, and the second, boiling at 228—232°/12—14 mm., had $\alpha_D^{19\cdot5} + 20\cdot32°$. The second fraction was then redistilled. The main product obtained boiled at the same temperature as before, and had $\alpha_D^{17\cdot5} + 20\cdot32°$. A Carius estimation with this specimen gave Cl = 41·10 per cent., and after another distillation the rotation was $\alpha_D^{15} + 20\cdot20°$, the chlorine content being 41·92 per cent. The theory for ethyl mono-trichloroacetyltartrate is 30·3, and for ethyl di-trichloroacetyltartrate 42·83 per cent., so that this substance was almost pure ethyl di-trichloroacetyltartrate. As the quantity of material was too small for further purification, the rotation of the ester was determined at a number of different temperatures, with these results:

Ethyl Di-trichloroacetyltartrate. [M = 497.]

t ...	20°	26·2°	36·5°	53°	70·7°	82·9°	15·2°	94°	131°
d ...	1·4714	1·4640	1·4515	1·4315	1·4100	1·3950	1·4770	1·3820	1·3355
$\alpha_D^{t°}$...	*19·85°*	+19·60°	19·36°	18·95°	18·33°	18·70°	19·74°	18·78°	18·85°
$[\alpha]_D^{t°}$	*13·49°*	+13·38°	13·35°	13·23°	13·35°	13·42°	13·56°	13·60°	14·10°
$[M]_D^{t°}$	*67·0°*	+66·5°	66·3°	66·7°	66·3°	66·7°	67·4°	67·6°	70·1°

It will be observed that the values both of specific or molecular rotation and of observed rotation gradually fall, to reach a minimum, and then rise again. The minimum value of the molecular rotation is + 66·0°, and it occurs at a temperature of 54°.

The data thus obtained may be compared with those for other similarly constituted substances, as in the table below:

	Acetyl-tartrate.		Monochloroacetyl-tartrate.		Dichloroacetyl-tartrate.		Trichloro-acetyltartrate.	
	$[\alpha]_D^{20}$.	$[M]_D^{20}$.	$[\alpha]_D^{20}$.	$[M]_D^{20}$.	$[\alpha]_D^{20}$.	$[M]_D^{20}$.	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
Ethyl mono-...	+9·36°*	+23·1°	11·44°‡	32·3°	—	—	15·5°†	54·7°
Ethyl di-	3·00 *	9·9	7·67 †	25·5	16·3°†	65·8°	13·5	67·1

For ethyl tartrate...... $[\alpha]_D^{20} + 7\cdot76°$; $[M]_D^{20} + 15\cdot86°$.

* McCrae and Patterson, Trans., 1900, **77**, 1100.

† Frankland and Patterson, Trans., 1898, **73**, 196.

‡ Frankland and Turnbull, Trans, 1898, **73**, 204.

As has been pointed out before (Trans., 1900, **77**, 1100) the introduction of the first acyl group into the ethyl tartrate molecule brings about a rise of rotation, whilst in passing to the disubstituted derivative a fall in rotation is observed. It will be noticed in the present case that so far as specific rotation is concerned, the regularity is maintained, but that it does not hold in regard to molecular rotation. A second regularity accounting for this is evident from the numbers in the table. The rise in molecular rotation on passing from ethyl tartrate to ethyl monoacetyltartrate is 7·24°, whilst in passing from this substance to ethyl diacetyltartrate the fall is 13·2°. In the monochloroacetyl series the rise is 16·44° and the fall only 6·8°. The initial rise thus becomes greater and the subsequent fall less as the number of chlorine atoms in the molecule increases, until in the trichloroacetyl series—and perhaps also in the dichloroacetyl series—this change has become a rise of 12·4°.

After the experiments just recorded, our specimen of ethyl di-trichloroacetyl tartrate was kept in a sealed tube for a year. On opening the tube after that time the rotation of the substance was $\alpha_{D}^{18\cdot8}+19\cdot63°$, which is practically identical with that originally found. A portion of the tartrate was then dissolved in nitrobenzene, and the rotation of the solution taken at several different temperatures, with the following results:

Ethyl Di-trichloroacetyltartrate in Nitrobenzene.

$p=4\cdot989$:

t	12·5°	15·4°	20°	52°	74·2°
d	1·2220	1·2190	1·2144	1·1827	1·1605
$\alpha_{D}^{t°}$	0·422°	0·418°	*0·424°*	0·435°	0·459°
$[\alpha]_{D}^{t°}$	+6·92°	6·87°	*7·00°*	7·37°	7·93°
$[M]_{D}^{t°}$	+34·4°	34·14°	*34·79°*	36·64°	39·4°

On heating to 110° the solution darkened a little in colour, so that no further observations could be made. The rotation is considerably lower in nitrobenzene than in the homogeneous condition. The data will be referred to again further on.

iso*Butyl Di-trichloroacetyltartrate.*—In order to ascertain whether larger alkyl radicles in the tartrate molecule would prevent—as we originally supposed the methyl and ethyl groups to do—the introduction of two trichloroacetyl radicles, we made three experiments in which *iso*butyl tartrate was heated with trichloroacetyl chloride. Of these we may describe the last. The ester (30 grams) was heated with 100 grams of the chloride under an inverted condenser for about thirty hours. After the excess of chloride had been removed, the residue showed signs of decomposition when an attempt was made to distil it under about 15 mm. pressure. The viscid liquid was therefore dissolved in chloroform, and this solution washed with water and dilute sodium carbonate solution. It was then dried over calcium chloride, and boiled for three hours with animal charcoal. The solution was filtered, and the chloroform removed. The residue still showed signs of decomposition when an attempt was made to distil it under 15 mm. pressure, but under 4 mm. it distilled readily. The crude product thus obtained was redistilled under 4 mm. pressure, and divided into three fractions, which all boiled at practically the same temperature, 208°. The rotations of these fractions differed very little, those of the first and second being slightly higher than the last. This, which was fully confirmed by the behaviour of the other two preparations, shows that in this case also the observed rotation of the monoacyl derivative is greater than that of the diacyl compound:

Found, Cl = 37·82.

$C_{16}H_{20}O_8Cl_6$ requires Cl = 38·52 per cent.

The rotation and density of this specimen were then determined at several different temperatures, with the following results:

iso*Butyl Di-trichloroacetyltartrate.* [M = 553.]

t	18·2°	20°	48·5°	75·8°	104·5°	131·5°	157°
d	1·3589	1·3550	1·3270	1·2980	1·2680	1·2400	1·2140
$\alpha_D^{t°}$	+22·7°	*22·56°*	21·54°	20·71°	20·14°	19·82°	19·57°
$[\alpha]_D^{t°}$	+16·7°	*16·65°*	16·23°	15·96°	15·88°	15·99°	16·12°
$[M]_D^{t°}$ ..	+92·4°	*92·1°*	89·8°	88·2°	87·8°	88·4°	89·2°

It will be observed that here again a distinct minimum occurs in the specific rotation curve at a temperature of 105°, when the value of the rotation is +15·9°, the corresponding value for the molecular rotation being +88°. The minimum has not yet appeared in the observed rotation; that it appears in the specific rotation is, of course, due to the fact that with rise of temperature the density becomes less, which causes the minimum to appear earlier in the specific rotation curve than in that for observed rotation.

The rotation of this ester was then determined in nitrobenzene solution, when the following numbers were found:

iso*Butyl Di-trichloroacetyltartrate in Nitrobenzene.*

$p = 5·024$:

t	13·6°	20°	26°	50·4°	91·9°
d	1·2166	1·2100	1·2040	1·1800	1·1390
$\alpha_D^{t°}$	+0·575°	*0·577°*	0·578°	0·615°	0·661°
$[\alpha]_D^{t°}$	+9·41°	*9·49°*	9·56°	10·37°	11·55°
$[M]_D^{t°}$	+52·0°	*52·5°*	52·8°	57·4°	63·9°

With these data it is possible to examine the effect of solution in nitrobenzene on these three esters of di-trichloroacetyltartaric acid. The relative numbers are given in the table below:

	$[M]^{20}_{D}$.		
Ester.	Homogeneous.	Nitrobenzene solution, $p=5$.	Δ.
Methyl di-trichloroacetyltartrate	—	$-15·2°$	—
Ethyl ,, ,, ...	67·0°	$+34·1$	32·9
*iso*Butyl ,, ,, ...	92·1	52·5	39·6

The influence in the two latter cases, and with almost absolute certainty in the first also, is to depress the rotation below the value for the homogeneous substance, and by amounts at least not far removed from each other. The effect of this solvent is thus of great interest, inasmuch as it increases the rotation of the simple esters like methyl tartrate and ethyl tartrate, but diminishes the rotation of their diacyl derivatives.

The chief interest attaching to the compounds we have described lies in the existence of a minimum in their temperature-rotation curves, this being, of course, exactly the same kind of phenomenon as the existence of a maximum. The first recorded instance of a minimum (maximum negative rotation) was in the case of ethyl dibenzoyltartrate (P. F. Frankland and Wharton, Trans., 1896, **69**, 1587); a minimum has been shown to exist in the temperature-rotation curve for menthol (maximum negative rotation) (Patterson and Taylor, Trans., 1905, **87**, 34), a maximum in that of ethyl tartrate (Patterson, Trans., 1908, **93**, 1884), whilst Pickard and Kenyon (Trans., 1911, **99**, 52, note) mention the occurrence of a minimum rotation in methyl-*n*-butyl- and methyl-*n*-octyl-carbinol, but the curves shown in their figure (*loc. cit.*, p. 50) seem very clearly to indicate the existence of a minimum in the specific rotation curves of practically all the alcohols examined by them. This question of the occurrence of maxima and minima in rotation curves is under investigation by one of us at the present time, and will be dealt with, it is hoped, in a future communication. Meanwhile, in regard to instances described in this paper we need only point out that the minimum observed in the specific rotation of the homogeneous ester apparently persists also in dilute nitrobenzene solution, but would be found at a temperature slightly below zero; thus the effect of nitrobenzene, which depresses the rotation of the esters, is to shift the minimum towards a lower temperature. This behaviour is thus somewhat similar to that which has been described by one of us (Trans., 1908, **93**, 1846) for ethyl tartrate in various solvents. In nitrobenzene, which greatly raises the rotation of the ester, the maximum specific rotation gradually moves, as the dilution increases, towards a higher value and a lower temperature.

We need only add that although the methyl, ethyl, and *iso*butyl esters of di-trichloroacetyltartaric acid may be prepared without any special difficulty, they nevertheless appear to be less stable than the corresponding esters of diacetyltartaric acid. They show a much greater tendency to decompose during preparation, and although the ethyl derivative remained undecomposed during a year in a sealed tube, the methyl ester on keeping in a stoppered bottle becomes somewhat soft—a specimen made seven years ago being now quite pasty—and the *iso*butyl ester on remaining for about six months in a corked tube deposited tartaric acid, the removal of which yielded a liquid almost devoid of activity.

We have, in conclusion, to express our thanks to Mr. J. F. Macdonald, M.A., B.Sc., Mr. A. McMillan, M.A., D.Sc., and Miss D. C. Patterson, each of whom carried out some of the work described in this paper.

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XLVII.—*Perhalides of Diphenyliodinium Iodide.*

By MARTIN ONSLOW FORSTER and JOHANNES HEINRICH SCHAEPPI.

THE discovery of phenyl iodochloride, $C_6H_5\cdot ICl_2$, by Willgerodt (*J. pr. Chem.*, 1886, [ii], **33**, 155), of iodosobenzoic acid by Victor Meyer and Wachter (*Ber.*, 1892, **25**, 2632), and of the diphenyliodinium bases by Hartmann and Victor Meyer (*Ber.*, 1894, **27**, 502 and 1592), re-directed attention to the remarkable facility with which iodine may be rendered multivalent in certain classes of organic compounds. Considerable developments have followed in this field, largely due to the first-named investigator and his collaborators, but it does not appear to have been noticed that the ionisable atom in diphenyliodinium iodide itself is capable of assuming fresh combining power quite as readily as the halogen in iodobenzene. It is true that in the latter paper by Hartmann and Victor Meyer already quoted, a di-iodide of diphenyliodinium iodide, $(C_6H_5)_2I\cdot I,I_2$, is described as arising when the iodinium iodide is treated with an alcoholic solution of iodine, thus recalling the periodides of alkylammonium bases, but as far as we have been able to ascertain, the substances described in the present communication have escaped notice.

When dry chlorine is passed into a suspension of diphenyliodinium iodide in chloroform, several stages of change in the appearance of the liquid may be recognised. The final product is a bright yellow, crystalline material, which resembles phenyl iodochloride in aspect, and was, indeed, at first mistaken for that substance, since analysis showed it to have the same empirical formula. Further examination, however, identified the compound as a tetrachloride of diphenyliodinium iodide, $(C_6H_5)_2I\cdot I,Cl_4$. The presence of the diphenyliodinium nucleus is established by the behaviour of this tetrachloride towards cold acetone, since it forms in this medium a clear solution, from which, after a brief interval, there separates a shower of colourless crystals consisting of diphenyliodinium chloride:

$$(C_6H_5)_2I\cdot I,Cl_4 \xrightarrow{\text{acetone}} (C_6H_5)_2I\cdot Cl + ICl_3.$$

Boiling water also converts the tetrachloride into diphenyliodinium chloride, setting free iodine and chlorine, there being produced at the same time a dichloride of diphenyliodinium iodide, $(C_6H_5)_2I\cdot I,Cl_2$, which, in turn, yields diphenyliodinium chloride by further action of water:

$$(C_6H_5)_2I\cdot I,Cl_2 \xrightarrow{\text{water}} (C_6H_5)_2I\cdot Cl + ICl.$$

Cold acetone converts the dichloride, also, into diphenyliodinium chloride, showing that the dichloride, like the tetrachloride, has retained the diphenyliodinium nucleus; as might be expected, it represents an intermediate stage in the production of the tetrachloride from diphenyliodinium iodide and chlorine. The conversion of the tetrachloride into the dichloride may be brought about also by interaction with the di-iodide, when the two substances, ground together in chloroform, are gently warmed:

$$2(C_6H_5)_2I\cdot I,Cl_4 + (C_6H_5)_2I\cdot I,I_2 = 3(C_6H_5)_2I\cdot I,Cl_2 + 2ICl,$$

and it may be reversed by the action of chlorine on the dichloride.

Before attempting to explain the course of the action, or series of actions, taking place when chlorine is passed into the chloroform suspension of diphenyliodinium iodide, it should be mentioned that one stage is marked by the separation of the di-iodide of diphenyliodinium iodide, a complication which could scarcely be foreseen. The di-iodide, in fact, appears to be the first intermediate product in the formation of the tetrachloride, and must be accompanied by diphenyliodinium chloride:

$$3(C_6H_5)_2I\cdot I + Cl_2 = (C_6H_5)_2I\cdot I,I_2 + 2(C_6H_5)_2I\cdot Cl.$$

The next step appears to be the conversion of the di-iodide into an iodochloride:

$$(C_6H_5)_2I{\cdot}I,I_2 + 2Cl_2 = (C_6H_5)_2I{\cdot}I,ICl + ICl_3,$$

which has been isolated, not only by arresting the action of chlorine at the proper stage, but also by interaction of the di-iodide and dichloride:

$$(C_6H_5)_2I{\cdot}I,I_2 + (C_6H_5)_2I{\cdot}I,Cl_2 = 2(C_6H_5)_2I{\cdot}I,ICl.$$

Following the production of this substance, the dichloride must ensue, and therefrom the tetrachloride:

$$(C_6H_5)_2I{\cdot}I,ICl + 2Cl_2 = (C_6H_5)_2I{\cdot}I,Cl_2 + ICl_3,$$
$$(C_6H_5)_2I{\cdot}I,Cl_2 + Cl_2 = (C_6H_5)_2I{\cdot}I,Cl_4.$$

It remains to account for the diphenyliodinium chloride, assumed to accompany the di-iodide of diphenyliodinium iodide in the preliminary stage, because the final product does not appear to contain it. We believe this to be explained by the fact that when the iodinium chloride is treated with a chloroform solution of iodine which has been saturated with chlorine, the tetrachloride of diphenyliodinium iodide separates:

$$(C_6H_5)_2I{\cdot}Cl + ICl_3 = (C_6H_5)_2I{\cdot}I,Cl_4.$$

Hence the non-appearance of the diphenyliodinium chloride in the final product must be due to its conversion into the tetrachloride by the iodine trichloride arising from the action of chlorine on the di-iodide. In this connexion it should be stated that diphenyliodinium chloride is not affected by chlorine alone.

The last observation seems to select the ionisable iodine atom in diphenyliodinium iodide as the one operative in the production of the perhalides, as although an equal partition of the chlorine between the two iodine atoms in the tetrachloride might, at first sight, appear probable, there does not seem to be any reason why diphenyliodinium chloride should not, in that case, yield at least a dichloride. In confirmation of this choice it is to be noted that perhalides comparable with some of those just described have been derived from tetramethylammonium iodide, a solution of which yields with chlorine the tetra-iodide, $(CH_3)_4NI,I_4$ (Weltzien, *Annalen*, 1856, **99**, 7); it is stated also by Dobbin and Masson (Trans., 1886, **49**, 849) that a dichloride, $(CH_3)_4NI,Cl_2$, is formed when tetramethylammonium iodide is warmed in an atmosphere of the halogen.

Passing now to the action of bromine on diphenyliodinium iodide, it has been found that the changes, although less complicated, are more difficult to follow by stages. The final product is the dibromide, $(C_6H_5)_2I{\cdot}I,Br_2$, convertible into the iodinium bromide, $(C_6H_5)_2I{\cdot}Br$, on dissolution in cold acetone. A slight modification of the conditions leads to the iodobromide, $(C_6H_5)_2I{\cdot}I,IBr$, which doubtless represents an intermediate stage in the formation of the dibromide. Although a tetrabromide is not formed, it seemed possible, in view of the existence of a tetrachloride, that the dibromide might associate itself with two atomic proportions of chlorine. On treating the substance in chloroform with the requisite amount of the halogen, however, a mixture of unchanged dibromide with the dichloride and tetrachloride was produced, nor could the expected dibromo-dichloride of diphenyliodinium iodide, $(C_6H_5)_2I{\cdot}I,Br_2,Cl_2$, be obtained by the action of bromine on the dichloride.

There remain only for consideration the products arising from diphenyliodinium chloride and bromide with iodine and bromine. Whilst bromine yields a dibromide with both the chloride and bromide, and iodine converts the iodinium bromide into a di-iodide, only one atomic proportion of iodine could be added to diphenyliodinium chloride; although this appears to contravene the rules of valency, there is no reason to suppose that the substance is a mixture, as it crystallised from a clear solution, and has been produced several times without revealing noticeable differences in properties or composition. Nevertheless, we are pursuing the subject in the hope of gaining some information respecting supplemental and partial valency.

Considerable obstacles have been encountered in the analysis of these materials. It was found impractible to estimate hydrogen owing to the difficulty of completely arresting the liberated iodine, even when much lead chromate was interposed. Accordingly, it has been the practice to ignore the hydrogen, and substitute for the tube in which water is usually collected a U-tube immersed in ice for the purpose of condensing the iodine which escaped from the combustion tube.

EXPERIMENTAL.

Tetrachloride of Diphenyliodinium Iodide, $(C_6H_5)_2I{\cdot}I,Cl_4$.

When dry chlorine was passed into chloroform containing diphenyliodinium iodide in suspension, the liquid gradually became brownish-red, and the salt dissolved; almost immediately dark brown crystals separated, but as the amount of chlorine increased, the brown colour of the solution diminished in intensity, and the crystals seemed to become colourless, or at most grey. Then a yellow colour was developed, and the solid, which was now so bulky as to fill the liquid, gradually became granular, and settled in the chloroform, which remained yellow. On recrystallising the product from chloroform, flat, yellow needles were deposited, melting at 118—120°:

0·1352 gave 0·1297 CO_2. C = 26·22.
0·2190 „ 0·4203 AgCl + AgI, giving 0·3458 AgCl. Cl = 25·88; I = 47·18.
$C_{12}H_{10}Cl_4I_2$ requires C = 26·18; Cl = 25·82; I = 46·18 per cent.

The same substance was produced when 2 grams of diphenyliodinium chloride mixed with 10 c.c. of dry chloroform were treated with 50 c.c. of the same solvent which had been saturated with chlorine after dissolving 0·7 gram of iodine.

Action of Acetone.—The tetrachloride when shaken with cold, dry acetone readily formed a clear, yellow solution, which in the course of a few seconds became filled with colourless crystals, melting and decomposing at about 225°; when an aqueous solution of this material was mixed with potassium iodide, precipitation of diphenyliodinium iodide occurred, whence it appeared that the iodinium chloride had been formed by the action of acetone on the tetrachloride.

Dichloride of Diphenyliodinium Iodide, $(C_6H_5)_2I{\cdot}I,Cl_2$.

On gently warming the tetrachloride with water, the liquid quickly became acid towards litmus, and gave a precipitate with silver nitrate. On continuing the heating until the water just boiled, there was formed a clear, pale brown solution, from which iodine vapour escaped, and on allowing it to cool, yellow spangles separated, melting at 136—137°; when crystallisation was complete, the mother liquor was colourless:

0·1332 gave 0·1468 CO_2. C = 30·06.
0·1703 „ 0·2643 AgCl + AgI, giving 0·1994 AgCl. Cl = 14·20; I = 52·86.
$C_{12}H_{10}Cl_2I_2$ requires C = 30·06; Cl = 14·82; I = 53·03 per cent.

Titration with sodium thiosulphate, following treatment of an alcoholic solution with potassium iodide, gave Cl = 14·51 per cent.

Although prepared by the action of hot water on the tetrachloride, the dichloride quickly suffers decomposition in the hot aqueous liquid, and cannot, therefore, be recrystallised conveniently in this way; it may, however, be recrystallised from alcohol, which deposits lustrous, golden plates, melting at the same temperature as the initial product. When the aqueous solution is boiled continuously, the yellow colour fades, crystals do not separate on cooling, and evaporation yields diphenyliodinium chloride (m. p. 227—229°, with decomposition. C = 45·3. $C_{12}H_{10}ClI$ requires C = 45·6 per cent.). If potassium iodide is added to an aqueous solution of the dichloride which has been warmed only long enough to dissolve the substance, a precipitate of the highly characteristic di-iodide described by Hartmann and Victor Meyer (*loc. cit.*) is produced.

The behaviour of the dichloride with acetone exactly resembles that of the tetrachloride, there being formed a clear yellow solution, from which diphenyliodinium chloride rapidly crystallises; as before, the acetone filtrate has a pungent odour, and finally becomes dark brown, so that iodoacetone and chloroacetone are most likely formed.

Iodochloride of Diphenyliodinium Iodide, $(C_6H_5)_2I{\cdot}I,ICl$.

On making attempts to recognise the iodochloride as an intermediate step in the transformation of the iodinium iodide into its tetrachloride, difficulty was experienced in isolating an individual substance. Arresting action at the stage when dark brown crystals separated, and recrystallising the product from alcohol after washing with carbon disulphide, the lustrous, dark red, almost black needles of the di-iodide were identified (m. p. 139—140°; $C=22{\cdot}08$. $C_{12}H_{10}I_4$ requires $C=21{\cdot}75$ per cent.). When the experiment was repeated, and the passage of chlorine continued very carefully beyond this stage, the crystals seemed to lose their colour, but this was found to be due to a change in structure, because on filtering them from the pale brown liquid they displayed a bronze lustre. After recrystallisation twice from alcohol, the dark brown substance melted at 134—135°, and was much paler than the di-iodide:

0·1936 gave 0·1819 CO_2. $C=25{\cdot}62$.
0·2840 „ 0·3961 $AgCl+AgI$, giving 0·2597 $AgCl$. $Cl=4{\cdot}01$; $I=66{\cdot}62$.
0·1568 gave 0·2275 $AgCl+AgI$, giving 0·1537 $AgCl$. $Cl=5{\cdot}99$; $I=65{\cdot}31$.
$C_{12}H_{10}ClI_3$ requires $C=25{\cdot}26$; $Cl=6{\cdot}08$; $I=66{\cdot}84$ per cent.

On treating this compound with acetone it was found to dissolve with greater difficulty than the dichloride and the tetrachloride; nevertheless, diphenyliodinium chloride is formed, as in the case of those two substances, but the separation of the salt begins before the dissolution of the iodochloride is complete. In this connexion it should be noted that the di-iodide also dissolves in acetone, forming a brownish-red solution, from which there is not any precipitation of diphenyliodinium iodide; the latter substance separates only when chlorine is passed into the liquid. Furthermore, when the di-iodide is covered with a mixture of acetone and chloroacetone, there is formed a brown solution, from which crystals of diphenyliodinium chloride slowly separate.

The iodochloride was prepared also by powdering a mixture of di-iodide and dichloride covered with alcohol, and warming on the water-bath until a clear solution was formed, when brown needles separated from the cold liquid and melted at 134—135°.

Dibromide of Diphenyliodinium Iodide, $(C_6H_5)_2I{\cdot}I,Br_2$.

Diphenyliodinium iodide (4 grams) suspended in chloroform was treated with a solution containing sufficient bromine (3·2 grams) to produce a tetrabromide; at first the substance darkened, but with further quantities of bromine the colour faded, and the final product was orange. Recrystallisation from alcohol gave beautiful, lustrous, orange plates, melting at 143°:

0·1713 gave 0·1574 CO_2. C = 25·07.
0·1285 „ 0·1894 AgBr + AgI. Br = 27·88; I = 44·27.
$C_{12}H_{10}Br_2I_2$ requires C = 25·35; Br = 28·17; I = 44·72 per cent.

On covering the dibromide with acetone, a yellow solution was rapidly formed, and almost immediately colourless crystals separated, melting and decomposing at 210°; this product was diphenyliodinium bromide.

Iodobromide of Diphenyliodinium Iodide, $(C_6H_5)_2I{\cdot}I,IBr$.

As already indicated, the isolation of an intermediate compound arising from the action of bromine on the iodinium iodide is much more difficult than when chlorine is used. It is possible to recognise the di-iodide as the first stage in the action, and when addition of bromine is continued, the expected iodobromide is certainly formed, although excess of the halogen converts this into the dibromide. Hence it is necessary to interrupt the treatment with bromine at a point subsequent to the formation of di-iodide and prior to its conversion into dibromide; this is very difficult, and attempts to do so frequently fail because the stages are not so clearly marked as in the case of chlorine. After several unsuccessful experiments there was obtained a product which could be freed from unchanged diphenyliodinium iodide by treatment with warm alcohol, the dark filtrate depositing slender, brown needles, melting at 121—122°:

0·0945 gave 0·0819 CO_2. C = 23·63.
0·1634 „ 0·2395 AgBr + AgI. Br = 13·15; I = 62·60.
$C_{12}H_{10}BrI_3$ requires C = 23·41; Br = 13·01; I = 61·95 per cent.

Just as the iodochloride of diphenyliodinium iodide when dissolved in acetone is converted into the iodinium chloride with loss of iodine, so the iodobromide is transformed into diphenyliodinium bromide.

Action of Iodine on Diphenyliodinium Chloride and Bromide.

In each case the salt was suspended in chloroform, to which there was gradually added a solution of iodine in the same solvent; the colour of the halogen was immediately destroyed, whilst the colourless salt became faintly brown, intensifying to chocolate. In the case of the chloride the suspended salt dissolved when the first portions of iodine were added, the iodide crystallising from the brown liquid; the bromide remained for the most part undissolved, changing into crystals of the di-iodide as the action proceeded. Attempts to recrystallise the products failed because the added halogen is so easily removed.

The *iodide* of diphenyliodinium chloride, $(C_6H_5)_2I{\cdot}Cl,I$, crystallised in small plates melting at 145—146°:

0·2017 gave 0·2373 CO_2. $C=32·09$.
0·1906 „ 0·2701 $AgCl+AgI$, giving 0·1909 $AgCl$. $Cl=8·67$; $I=57·64$.
$C_{12}H_{10}ClI_2$ requires $C=32·51$; $Cl=7·97$; $I=57·34$ per cent.

On mixing a weighed quantity with potassium iodide and acetic acid, titration with sodium thiosulphate after an interval of twelve hours gave results in agreement with one atomic proportion of iodine only to diphenyliodinium chloride. As might be expected from the behaviour of the substances previously described, the last-named salt is regenerated when the iodide is dissolved in acetone.

The *di-iodide* of diphenyliodinium bromide, $(C_6H_5)_2I{\cdot}Br,I_2$, crystallised also in small plates, somewhat darker than those of the foregoing salt, and melting at the same temperature:

0·0877 gave 0·0790 CO_2. $C=24·56$.
0·1096 „ 0·1565 $AgBr+AgI$. $Br=12·81$; $I=60·98$.
$C_{12}H_{10}BrI_3$ requires $C=23·41$; $Br=13·01$; $I=61·95$ per cent.

Titration with sodium thiosulphate revealed the presence of two atomic proportions of iodine added.

Action of Bromine on Diphenyliodinium Chloride and Bromide.

When the chloride suspended in chloroform was subjected to the action of bromine, there was produced a clear, orange-coloured solution, from which slender, orange needles quickly separated; the iodinium bromide in similar circumstances did not dissolve, but changed into an orange-coloured, crystalline product.

The *dibromide* of diphenyliodinium chloride, $(C_6H_5)_2I{\cdot}Cl,Br_2$, melted at 127—128°:

0·2045 gave 0·2227 CO_2. C = 29·70.
0·2017 „ 0·3184 AgCl + AgBr + AgI. Cl = 7·42 ; Br = 33·51 ; I = 26·58.

$C_{12}H_{10}ClBr_2I$ requires C = 30·25 ; Cl = 7·45 ; Br = 33·61 ; I = 26·66 per cent.

Titration with sodium thiosulphate following addition of potassium iodide and acetic acid gave results corresponding with the presence of two available atoms of bromine.

The *dibromide* of diphenyliodinium bromide, $(C_6H_5)_2I·Br,Br_2$, melted at 147—148°:

0·2144 gave 0·2213 CO_2. C = 28·15.
0·2489 „ 0·3817 AgBr + AgI. Br = 46·11 ; I = 24·38.
$C_{12}H_{10}Br_3I$ requires C = 27·64 ; Br = 46·06 ; I = 24·36 per cent.

The titration with sodium thiosulphate corroborated the presence of two added atomic proportions of bromine.

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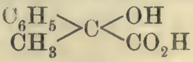
XLVIII.—*Experiments on the Walden Inversion. Part VIII. a-Amino-a-phenylpropionic Acids.*

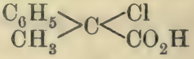
By Alex. McKenzie and George William Clough.

The interconversion of the optically active α-hydroxy-α-phenylpropionic acids (atrolactinic acids) has been described in a former communication (Trans., 1910, **97**, 1016). The *l*-acid (I), for example, was converted by thionyl chloride into *l*-α-chloro-α-phenylpropionic acid (II), from which the *d*-hydroxy-acid was obtained by means of silver oxide and water. The chlorine in the optically active chloro-acids was also displaced with great facility by shaking with water at the ordinary temperature, and the atrolactinic acid obtained in this manner was optically inactive.



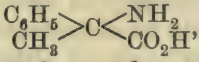
$$\begin{matrix}C_6H_5\\CH_3\end{matrix}\!>C<\!\begin{matrix}OH\\CO_2H\end{matrix}$$

(I.)



$$\begin{matrix}C_6H_5\\CH_3\end{matrix}\!>C<\!\begin{matrix}Cl\\CO_2H\end{matrix}$$

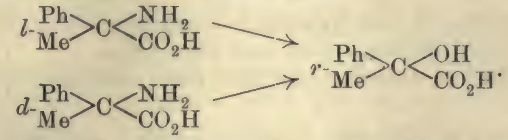
(II.)

In consequence of these observations the authors have now examined the corresponding amino-acids,  $\begin{matrix}C_6H_5\\CH_3\end{matrix}\!>C<\!\begin{matrix}NH_2\\CO_2H\end{matrix}$, the study of which has a certain amount of interest, inasmuch as no amino-acid containing a tertiary asymmetric carbon atom has hitherto been studied with reference to the Walden inversion.

It was necessary in the first place to resolve the *dl*-compound into its active components, and for this purpose the well-known device of E. Fischer for the resolution of *dl*-amino-acids was adopted. The acid was converted into its formyl derivative, from which the active forms were obtained by aid of cinchonidine and quinine. The amino-acids were then prepared by hydrolysing the active formyl compounds with hydrobromic acid. The following values were obtained:

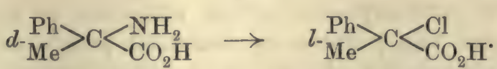
	$[\alpha]_D$.	
d-α-Formylamino-α-phenylpropionic acid	+91·9°	in ethyl-alcoholic solution.
l- ,, ,, ,,	−91·6	,, ,, ,,
d-α-Amino-α-phenylpropionic acid	+70·0	in aqueous solution.
l- ,, ,, ,,	−69·5	,, ,,

Complete racemisation took place with the formation of *r*-atrolactinic acid, when the amino-group was displaced by the hydroxy-group by means of nitrous acid, thus:



$$l\text{-}\begin{smallmatrix}\text{Ph}\\ \text{Me}\end{smallmatrix}\!>\!\text{C}\!<\!\begin{smallmatrix}\text{NH}_2\\ \text{CO}_2\text{H}\end{smallmatrix} \longrightarrow r\text{-}\begin{smallmatrix}\text{Ph}\\ \text{Me}\end{smallmatrix}\!>\!\text{C}\!<\!\begin{smallmatrix}\text{OH}\\ \text{CO}_2\text{H}\end{smallmatrix}.\longleftarrow d\text{-}\begin{smallmatrix}\text{Ph}\\ \text{Me}\end{smallmatrix}\!>\!\text{C}\!<\!\begin{smallmatrix}\text{NH}_2\\ \text{CO}_2\text{H}\end{smallmatrix}$$

Again, when the *d*-amino-acid was acted on by a mixture of fuming hydrochloric acid and sodium nitrite, the racemisation was practically complete, the activity observed being very slight and in the lævo-direction. It is probable that the following change had occurred:



$$d\text{-}\begin{smallmatrix}\text{Ph}\\ \text{Me}\end{smallmatrix}\!>\!\text{C}\!<\!\begin{smallmatrix}\text{NH}_2\\ \text{CO}_2\text{H}\end{smallmatrix} \longrightarrow l\text{-}\begin{smallmatrix}\text{Ph}\\ \text{Me}\end{smallmatrix}\!>\!\text{C}\!<\!\begin{smallmatrix}\text{Cl}\\ \text{CO}_2\text{H}\end{smallmatrix}.$$

Those changes in which the amino-group is displaced by hydroxy- and chlorine groups respectively, provide another example of the profound racemisation which occurs when substitution is effected in a compound with a phenyl group directly attached to the asymmetric carbon atom (compare Trans., 1908, **93**, 811; 1909, **95**, 777, and *loc. cit.*). It is also possibly of some significance that the racemisation phenomena are so pronounced in the transformations undergone by compounds which do not contain a hydrogen atom directly attached to the asymmetric carbon atom. Bearing in mind, however, that atrolactinic acid and its derivatives are the only compounds of the latter type which have been brought within the scope of this investigation, it would be necessary to examine the effect produced by varying the hydrocarbon residues attached to the asymmetric atom before any general conclusion could be drawn on this point.

When a group attached to an asymmetric carbon atom is substituted by another group, a certain amount of racemisation accompanies the change with a regularity that can hardly be accidental. The authors have come to the conclusion that such a substitution is *invariably* accompanied by racemisation irrespective of whether a configuration change takes place or not. The work of E. Fischer provides numerous examples bearing on this point, and, so far as the contributions of the present series of papers are concerned, the following changes may be referred to:

(1) Conversion of *l*-mandelic acid into (*a*) *d*-phenylchloroacetic acid by phosphorus pentachloride, and (*b*) *l*-phenylchloroacetic acid by thionyl chloride.

(2) Action of water on (*a*) *l*-phenylchloroacetic acid, and (*b*) salts of this acid.

(3) Conversion of *l*-phenylchloroacetic acid into (*a*) *l*-phenylmethoxyacetic acid, and (*b*) *d*-phenylaminoacetic acid.

(4) Conversion of *l*-phenylaminoacetic acid into (*a*) *d*-mandelic acid, and (*b*) *d*-phenylchloroacetic acid.

(5) Conversion of *l*-β-hydroxy-β-phenylpropionic acid into *d*-β-bromo-β-phenylpropionic acid and vice versa.

(6) Conversion of *l*-atrolactinic acid into *r*-α-chloro-α-phenylpropionic acid.

(7) Conversion of *l*-α-bromo-β-phenylpropionic acid into *l*-α-hydroxy-β-phenylpropionic acid.

(8) Action of phosphorus pentachloride and of thionyl chloride on hydroxy-acids and esters; etc.

The preparation of an optically pure compound from the product resulting from such displacements can sometimes be effected quite readily, but for this purpose an analytical process is necessary; thus in the preparation of *d*-α-chloro-α-phenylpropionic acid from *d*-atrolactinic acid by the action of thionyl chloride, the crude product is drained on porous plate, and then crystallised from light petroleum, an operation which removes the *r*-chloro-acid present.

Walden's early conception of "die directe Umwandlung (ohne vorausgegangene Racemisirung) des einen optischen Isomeren in seinen Antipoden" (*Ber.*, 1896, **29**, 138) requires therefore to be modified. The racemisation phenomena upon which emphasis is laid in the present communication are in harmony with the picture recently presented by E. Fischer in his discussion of the close bearing of the Walden inversion on the nature of substitution in organic compounds in general (*Annalen*, 1911, **381**, 123; 1912, **386**, 374); they are also taken into account by Werner (*Ber.*, 1911, **44**, 873; *Annalen*, 1911, **386**, 65).

EXPERIMENTAL.

dl-*α-Amino-α-phenylpropionic Acid.*

Eighty grams of powdered potassium cyanide were moistened with 5 c.c. of water, and 100 grams of acetophenone were added. The mixture was surrounded with ice-cold water, and the addition of 90 c.c. of fuming hydrochloric acid (D 1·2) was conducted within an interval of five hours. The slight excess of hydrogen cyanide was found to be advantageous.* After thirty minutes the crude cyanohydrin was converted into *dl*-*α*-amino-*α*-phenylpropionic acid (*α*-aminohydratropic acid) by heating with ethyl-alcoholic ammonia at 70° in a pressure flask (compare Tiemann and Köhler, *Ber.*, 1881, **14**, 1980). The yield amounted to 50 grams.

The acid sublimes without melting at 268—270°, and exhibits the properties already described by Tiemann and Köhler. It is sparingly soluble in cold water, 100 grams of the latter at 22° dissolving about 4·8 grams of the acid.

Resolution of dl-*α-Formylamino-α-phenylpropionic Acid.*

The formyl acid was prepared in the following manner. *dl*-*α*-Amino-*α*-phenylpropionic acid (60 grams) was mixed with anhydrous formic acid (90 grams), the resulting solid becoming liquid when heated on a water-bath. After four hours' heating, the excess of formic acid was removed under diminished pressure, and the residual solid heated with 90 grams of formic acid for four hours. This treatment was repeated twice. The product was a viscid oil, which solidified when kept over soda-lime and under diminished pressure. It was ground under 150 c.c. of ice-cold *N*-hydrochloric acid in order to remove unchanged amino-acid, drained, and washed with ice-cold water. The yield was 35 grams. As the acid was slightly coloured, it was purified by boiling with 500 c.c. of water and a little animal charcoal.

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* This mode of forming acetophenonecyanohydrin was previously (Trans., 1910, **97**, 1018) adopted by the authors for the purpose of obtaining atrolactinic acid by modifying Spiegel's method (*Ber.*, 1881, **14**, 1353). In view, however, of a recent publication by Staudinger and Ružička (*Annalen*, 1911, **380**, 278) on phenylmethylketen, for the preparation of which atrolactinic acid was used, it may not be superfluous to give details which were not described formerly.

The cyanohydrin was prepared in the above-mentioned manner. It was dissolved in 200 c.c. of fuming hydrochloric acid (D 1·2) at 0°, and the solution maintained at 0° for one hour and then at the ordinary temperature for twelve hours. No ammonium chloride separated. Air was blown through the liquid for some time, an excess of sodium hydroxide was added, and the mixture was submitted to steam distillation in order to remove unattacked acetophenone and to hydrolyse the amide present. The atrolactinic acid was then precipitated by mineral acid and collected, whilst the filtrate was extracted once with ether, when an additional 6 grams of acid were obtained. The acid was crystallised once from water. The yield of the crystallised acid was 60 grams, which corresponds with 43 per cent. of the acetophenone used.

Spiegel's method was abandoned as unsatisfactory by Staudinger and Ružička and also by Lennart Smith (*J. pr. Chem.*, 1911, [ii], **84**, 731), the yield of acid being small.

dl-*α-Formylamino-α-phenylpropionic acid*,

$$CHO{\cdot}NH{\cdot}CMePh{\cdot}CO_2H,$$

is sparingly soluble in cold water, and separates in clusters of colourless, microscopic needles. It is practically insoluble in benzene, light petroleum, chloroform, carbon tetrachloride, or ether, moderately soluble in boiling, but sparingly so in cold ethyl acetate, and readily so in hot acetone. It is very soluble in boiling methyl alcohol or ethyl alcohol, and fairly so in these solvents at the ordinary temperature. It melts and decomposes at 178—179°. For analysis, it was dried over sulphuric acid in a vacuum:

0·1845 gave 0·4218 CO_2 and 0·0960 H_2O. C = 62·3; H = 5·8.

$C_{10}H_{11}O_3N$ requires C = 62·1; H = 5·7 per cent.

Preliminary experiments with various alkaloids indicated that the resolution of the *dl*-acid into its optically active isomerides could be effected with quinine or cinchonidine. Since the quinine *d*-salt is considerably more sparingly soluble in water than is the quinine *l*-salt, the *d*-acid can readily be obtained by the aid of quinine. On the other hand, the cinchonidine *l*-salt is more sparingly soluble than the cinchonidine *d*-salt. Accordingly, the mother liquors from the resolution by quinine which contain a preponderance of quinine *l*-salt give, after removal of the alkaloid, a mixture of *d*- and *l*-acids containing an excess of the latter. This mixture is then converted into cinchonidine salt, and the pure cinchonidine *l*-salt is then easily obtained. The following description is typical of the resolution.

dl-α-Formylamino-*α*-phenylpropionic acid (19·3 grams, 1 mol.) was dissolved in two litres of hot water, and anhydrous quinine (32·4 grams, 1 mol.) added. Boiling was continued until the alkaloid had dissolved completely. The crystals which separated on remaining for twenty-four hours in an ice-chest amounted to 25 grams, and, when this product was crystallised from 1500 c.c. of boiling water, 18 grams of a salt separating in clusters of long, silky needles were obtained. After trituration with 100 c.c. of *N*-sodium carbonate and extraction of the liberated quinine with ether, concentrated hydrochloric acid was added gradually until no further precipitate was produced, and the mixture was then surrounded with ice-cold water for half-an-hour. The acid was then separated, and washed with a little water. It was practically pure, and amounted to 6·1 grams. It was further crystallised from

150 c.c. of water, and after cooling in ice-cold water 4·6 grams of the pure *d*-acid were obtained. On concentration of the mother liquor under diminished pressure at the ordinary temperature an additional 0·5 gram was obtained.

d-*α-Formylamino-α-phenylpropionic acid* is more sparingly soluble in cold water than is the *dl*-isomeride, and separates in tiny, feathery, colourless needles. It melts and decomposes at 194—195°. For analysis it was dried over sulphuric acid in a vacuum:

0·1574 gave 0·3590 CO_2 and 0·0792 H_2O. C = 62·2; H = 5·6.

$C_{10}H_{11}O_3N$ requires C = 62·1; H = 5·7 per cent.

A solution of 0·4626 gram in 2·4 c.c. of *N*-sodium hydroxide was made up to 10 c.c. with water, and gave α_D^{15} +12·04° in a 2-dcm. tube, whence $[\alpha]_D^{15}$ +130·1°, this value being calculated on the weight of acid taken.

In ethyl-alcoholic solution:

$l = 2$, $c = 3{\cdot}214$, α_D^{16} +5·91°, $[\alpha]_D^{16}$ +91·9°.

The first mother liquor from the crystallisation of the quinine salt was concentrated under reduced pressure at 40—60° to about 300 c.c., the quinine precipitated by sodium carbonate, and the filtrate again concentrated. The solution was then cooled in ice, and the formyl acid precipitated by means of concentrated hydrochloric acid. The yield of acid was 6·5 grams, of which 0·302 gram, when dissolved in 1·6 c.c. of *N*-sodium hydroxide and made up with water to 10 c.c., gave α_D −4·80° in a 2-dcm. tube, whence $[\alpha]_D$ −79·5°. The second mother liquor from the crystallisation of the quinine salt, when treated in a manner similar to the preceding, also gave a lævorotatory acid (1·3 grams) with $[\alpha]_D$ −60°. The lævorotatory mixture of formyl acids (7·5 grams, 1 mol.), obtained by uniting the acids with $[\alpha]_D$ −79·5° and −60°, was dissolved in 500 c.c. of boiling water, and cinchonidine (11·4 grams, 1 mol.) was added. On cooling, silky needles soon began to separate, and after six hours at the ordinary temperature the crystals (13 grams) were removed. The salt was triturated with 50 c.c. of 2*N*-hydrochloric acid, and the formyl acid drained off as soon as a sample of the solid dissolved entirely in sodium hydroxide. The yield of acid was 4·8 grams, and after crystallisation from 120 c.c. of water 3·3 grams of the pure *l*-acid were obtained.

l-*α-Formylamino-α-phenylpropionic acid* separates from water in feathery needles, and melts and decomposes at 194—195°. For analysis it was dried over sulphuric acid in a vacuum:

0·2032 gave 0·4635 CO_2 and 0·1070 H_2O. C = 62·2; H = 5·9.

$C_{10}H_{11}O_3N$ requires C = 62·1; H = 5·7 per cent.

A solution of 0·3065 gram in 1·6 c.c. of *N*-sodium hydroxide was made up to 10 c.c. with water, and then gave α_D^{20} −7·85° in a 2-dcm.

tube, whence $[\alpha]_D^{20}$ $-128{\cdot}1°$, this value being calculated on the weight of acid taken.

In ethyl-alcoholic solution:

$$l=2,\ c=3{\cdot}762,\ \alpha_D^{17}\ -6{\cdot}89°,\ [\alpha]_D^{17}\ -91{\cdot}6°.$$

The *l*-acid can also be prepared, without the use of cinchonidine, from the mother liquors resulting from the crystallisation of the quinine *d*-salt, but this method is less convenient than the one described. That the pure *d*- and *l*-acids were obtained was clear from the fact that the values for the specific rotation of the acids prepared from several separate resolutions were practically identical, and repeated crystallisation of the acids had no effect in raising the values.

Hydrolysis of the Optically Active α-Formylamino-α-phenylpropionic Acids.

Four grams of *d*-α-formylamino-α-phenylpropionic acid were boiled for half-an-hour with 40 c.c. of *N*-hydrobromic acid under a reflux condenser. After the excess of acid had been distilled off by heating in a vacuum, the amino-acid hydrobromide crystallised out in glassy prisms. The salt was dissolved in 15 c.c. of ethyl alcohol, and the amino-acid precipitated by the addition of ethyl-alcoholic ammonia. The resulting acid was freed from the small amount of ammonium bromide present by crystallisation from water. Yield 3·1 grams.

d-*α-Amino-α-phenylpropionic acid* (*α-aminohydratropic acid*), $NH_2{\cdot}CMePh{\cdot}CO_2H$, crystallises from water in colourless, glassy prisms, and after drying at 100° sublimes at about 295°:

0·1385 gave 0·3314 CO_2 and 0·0850 H_2O. C = 65·3; H = 6·9.

$C_9H_{11}O_2N$ requires C = 65·4; H = 6·7 per cent.

0·3946 Gram, made up to 10 c.c. with *N*-hydrochloric acid, gave α_D^{18} $+7{\cdot}11°$ in a 2-dcm. tube, whence $[\alpha]_D^{18}$ $+90{\cdot}1°$, this value being calculated on the weight of acid taken.

In aqueous solution:

$$l=2,\ c=2{\cdot}02,\ \alpha_D^{18}\ +2{\cdot}83°,\ [\alpha]_D^{18}\ +70{\cdot}0°.$$

The acid is sparingly soluble in cold water, 100 parts of the latter at 22° dissolving about 3·2 parts of the acid. The active acid is thus somewhat less soluble than the inactive isomeride at the ordinary temperature. It is practically insoluble in all the commoner organic solvents. Its aqueous solution gives a deep blue coloration with copper sulphate.

l-*α-Amino-α-phenylpropionic acid*, prepared by the hydrolysis of its formyl derivative with hydrobromic acid, crystallises from water in glassy prisms, and sublimes at about 295°:

0·1413 gave 0·3356 CO_2 and 0·0838 H_2O. C=64·8; H=6·6.

$C_9H_{11}O_2N$ requires C=65·4; H=6·7 per cent.

0·274 Gram, made up to 10 c.c. with *N*-hydrochloric acid, gave α_D^{19} −4·95° in a 2-dcm. tube, whence $[\alpha]_D^{19}$ −90·3°, this value being calculated on the weight of acid taken.

In aqueous solution:

$$l=2,\ c=1{\cdot}82,\ \alpha_D^{20}\ -2{\cdot}53°,\ [\alpha]_D^{20}\ -69{\cdot}5°.$$

Action of Nitrous Acid on the Active Amino-acids.

A solution of the *l*-amino-acid (2·1 grams) in 15 c.c. of *N*-hydrochloric acid was cooled in ice, and a solution of 1·5 grams of sodium nitrite in 3 c.c. of water added drop by drop within an interval of one and a-half hours. The liquid remained in ice for two hours longer, and then at the ordinary temperature for two hours, by which time the evolution of gas had ceased. Water was added to make up the solution to 20 c.c., the whole of which on polarimetric examination in a 4-dcm. tube was found to be optically inactive. It was then extracted with ether. The aqueous portion was inactive, and the acid obtained from the ethereal extract was also inactive in ethyl-alcoholic solution. The latter acid (1·7 grams) was identified as *r*-α-hydroxy-α-phenylpropionic (atrolactinic) acid by its melting point and analysis.

The *d*-amino-acid gave a similar result when acted on by nitrous acid.

Action of a Mixture of Fuming Hydrochloric Acid and Sodium Nitrite on the d-*Amino-acid.*

One and a-half grams of the powdered *d*-amino-acid were added to 20 c.c. of fuming hydrochloric acid (saturated at 0°). The hydrochloride of the amino-acid separated. A solution of 1·5 grams of sodium nitrite in 3 c.c. of water was added within an interval of two hours, the temperature being maintained at 0°. After remaining for an additional three hours, the mixture was diluted with water (20 c.c.), and extracted quickly with ether. The resulting acid amounted to 0·9 gram, and dissolved readily in 8 c.c. of benzene; the solution was feebly lævorotatory, giving α_D −0·15° in a 2-dcm. tube. Analysis showed that the acid consisted mainly of *r*-α-chloro-α-phenylpropionic acid, but it was not clear whether the lævorotation referred to was due to a trace of the lævorotatory chloro-acid or to atrolactinic acid.

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XLIX.—*Chemical Examination of Scammony Root and of Scammony.*

By FREDERICK BELDING POWER and HAROLD ROGERSON.

THE gum-resin obtained by incision from the living root of *Convolvulus Scammonia*, Linné (Nat. Ord. *Convolvulaceae*), and commonly designated as scammony or "virgin scammony," has been known and used medicinally for many centuries (compare "Pharmacographia," 2nd edit., p. 439). The value of this product depends on its resinous constituent, which, however, is now most frequently prepared by extracting the dried scammony root with alcohol, and precipitating the resin with water. The resin of scammony, as obtained from either of these sources, is still recognised by several of the national Pharmacopœias, although at the present time it appears to have been displaced to a large extent by the resin from the root of *Ipomoea orizabensis*, Ledanois—commonly known as "Mexican Scammony Root," the two products being generally regarded as chemically identical (compare this vol., p. 1). The term "scammonin," as applied to the resin of scammony, is therefore considered to be synonymous with the "jalapin" of Mayer (*Annalen*, 1855, **95**, 129), which designates the ether-soluble resin of the above-mentioned species of *Ipomoea*.

Considerable attention has hitherto been devoted to the sugars contained in scammony root, and especially to those produced by the hydrolysis of scammony resin and "jalapin" (compare Votoček, *Zeitsch. Zuckerind. Böhm.*, 1903, **27**, 257; 1905, **30**, 20, 117; *Ber.*, 1904, **37**, 3859, 4615; Requier, *J. Pharm. Chim.*, 1904, [vi], **20**, 148, 213; 1905, [vi], **22**, 435, 492, 540). Apart from these products, however, the previously recorded investigations pertaining to scammony root or its resin have been either of a somewhat fragmentary nature or based on the erroneous assumption that the resin is a homogeneous substance.

One of the earliest investigations of scammony resin was by Johnston (*Phil. Trans.*, 1840, Part II., p. 341), who assigned to the product obtained from the gum-resin known as scammony the formula $C_{40}H_{33}O_{20}$, or, according to present notation, $C_{20}H_{33}O_{10}$. Keller (*Annalen*, 1857, **104**, 63; 1859, **109**, 209) gave to "scammonin" the formula $C_{38}H_{64}O_{16}$, whereas Spirgatis (*Annalen*, 1860, **116**, 289, and *Arch. Pharm.*, 1894, **232**, 241, 482) believed it to possess the formula $C_{34}H_{56}O_{16}$, which is the same as that assigned by Mayer to "jalapin" (*loc. cit.*, and this vol., p. 2). Kromer (*J. Chem. Soc.*, 1893, **64**, i, 423) considered scammony resin to be represented by the formula $C_{88}H_{156}O_{42}$. These discrepancies of statement respecting the ultimate composition of scammony resin may, however, readily be understood if it be considered that, like other similar products from convolvulaceous plants, it does not represent an individual substance, but is a somewhat complex mixture.

Inasmuch as the present authors have recently made a complete investigation of the resin of *Ipomoea orizabensis* (this vol, p. 1), with which, as already noted, the resin of scammony has been presumed to be identical, it was deemed desirable to subject the latter to a comparative examination. For this purpose the resin was prepared directly from the root, and also from the product known as virgin scammony.

EXPERIMENTAL.

I.—*Examination of Scammony Root.*

The material employed consisted of a good quality of Levant scammony root (from *Convolvulus Scammonia*, Linné).

As a preliminary experiment, 50 grams of the ground material were successively extracted in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried at 100°, were obtained:

Petroleum (b.p. 40—60°)	extracted	0·32 gram	= 0·64 per cent.
Ether	,,	4·00 ,,	= 8·00 ,, ,,
Chloroform	,,	0·38 ,,	= 0·76 ,, ,,
Alcohol	,,	4·50 ,,	= 9·00 ,, ,,
	Total......	9·20 grams	= 18·40 per cent.

Determination of the Total Resin.—Fifty grams of the ground material were completely extracted in a Soxhlet apparatus with hot alcohol. To the liquid thus obtained 25 c.c. of water were added, the alcohol then evaporated, and the separated resin thoroughly washed with hot water, after which it was dried in a water-oven until of constant weight. The mean of two nearly concordant determinations was an amount equivalent to 9·65 per cent. of resin in the root. The proportion of this crude resin which was soluble in ether, as determined by its complete extraction in a Soxhlet apparatus, was equivalent to 97 per cent. of its weight.

Extraction of the Root with Alcohol.

For the purpose of a complete examination of the constituents of the root, a quantity (50·35 kilograms) of the ground material was extracted by continuous percolation with hot alcohol. After the removal of the greater portion of the alcohol, 13·89 kilograms of a soft, dark-coloured extract were obtained.

Isolation of Sucrose.

Inasmuch as sucrose has previously been isolated from scammony root by Requier (*J. Pharm. Chim.*, 1905, [vi], **22**, 435, 492), it was deemed desirable to ascertain its presence in the root under examination. For this purpose a quantity (500 grams) of the above-mentioned alcoholic extract was mixed with water to separate the resin, the dark-coloured aqueous liquid filtered, and treated with an excess of milk of lime. The mixture was then filtered, the alkaline filtrate saturated with carbon dioxide, again filtered, and the clear liquid evaporated under diminished pressure to the consistency of a syrup. By treating the latter with successive portions of alcohol a product was finally obtained, which was completely soluble in alcohol of about 85 per cent. strength. The solution of this product, when decolorised by a little animal charcoal and inoculated with a trace of sucrose, gradually deposited a quantity (1·4 grams) of a crystalline substance. After recrystallisation from dilute alcohol, the substance was obtained in small, colourless prisms, melting at 184—185° (compare this vol., p. 4), and was identified as sucrose. (Found, $C=41{\cdot}9$; $H=6{\cdot}5$. Calc., $C=42{\cdot}1$; $H=6{\cdot}4$ per cent.)

Distillation of the Extract with Steam: Separation of an Essential Oil.

A quantity (2·3 kilograms) of the alcoholic extract was mixed with water, and distilled in a current of steam. The distillate, which contained some oily drops, was extracted with ether, the ethereal liquid being dried and the solvent removed, when a small amount (0·35 gram) of an essential oil was obtained. This had a reddish-yellow colour, a persistent odour, and gave the colour reaction for furfuraldehyde.

After the above-described operation, there remained in the distillation flask a dark-coloured aqueous liquid (A) and a quantity of a soft resin (B). The resin was repeatedly washed with hot water until the latter remained colourless, and the washings added to the main portion of aqueous liquid.

Examination of the Aqueous Liquid (A).

Isolation of Scopoletin, $(CH_3\cdot O)(OH)C_6H_2\cdot CH{:}CH\cdot CO\cdot O$.

The aqueous liquid was concentrated under diminished pressure, and extracted with ether, which, however, removed only a small quantity of resinous material and a trace of fluorescent substance.

It was then extracted many times with chloroform, and the chloroformic liquids shaken with aqueous sodium carbonate, which removed practically all of the dissolved substance. On acidifying the alkaline liquid, a quantity (0·25 gram) of a crystalline substance was precipitated. This was dissolved in chloroform, the solvent evaporated, and the residue recrystallised from absolute alcohol, when the substance separated in pale yellow needles melting at 203—204°. With alkalis it gave a brilliant blue fluorescence, and was identified as scopoletin. (Found, C = 62·5; H = 4·4. Calc., C = 62·5; H = 4·2 per cent.) Its identity was further confirmed by the preparation of the acetyl derivative melting at 176—177°.

Isolation of 3:4-*Dihydroxycinnamic Acid*,
$C_6H_3(OH)_2 \cdot CH:CH \cdot CO_2H$.

The original aqueous liquid, which had been extracted with ether and chloroform as above described, was next shaken with successive portions of amyl alcohol. The amyl-alcoholic liquids were then united, washed with a little water, and distilled under diminished pressure, when a quantity of a dark-coloured, syrupy product was obtained. This was heated for a few minutes with a 10 per cent. solution of potassium hydroxide, the alkaline liquid being then acidified and extracted with ether. The ethereal liquid was subsequently shaken with aqueous ammonium carbonate, and the alkaline liquid acidified, when a quantity (15 grams) of a crystalline substance was precipitated. When recrystallised from very dilute alcohol, it separated in pale yellow, prismatic needles, which melted and decomposed at 223—225°, and its aqueous solution gave a dark green colour with ferric chloride. An analysis of the substance proved it to be 3:4-dihydroxycinnamic acid * (Found, C = 59·7; H = 4·6. Calc., C = 60·0; H = 4·4 per cent.), and its identity was further confirmed by the preparation of the dimethyl ether melting at 180—181°.

After extracting the aqueous liquid with the above-mentioned solvents, it was heated in a current of steam for the removal of the last traces of amyl alcohol, and to the warm liquid a slight excess of a solution of basic lead acetate was added, when a copious yellow precipitate was produced. This was collected, washed, then suspended in water, and decomposed by hydrogen sulphide. After filtering the mixture, concentrating the filtrate under diminished pressure, and treating the residue with a solution of potassium hydroxide, a further small amount of 3:4-dihydroxycinnamic acid was obtained.

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* It may be noted in this connexion that in our previous investigation of Jalap (*J. Amer. Chem. Soc.*, 1910, **32**, 80) it was not observed that 3:4-dihydroxycinnamic acid is a constituent of the drug. Through the kindness of Messrs. W. Ransom & Son, of Hitchin, who have supplied us with material for further examination, we have now been able to ascertain that the respective acid is also contained in Jalap tubers, although apparently in much smaller amount than in the roots of Scammony and *Ipomoea orizabensis*.

The filtrate from the precipitate produced by basic lead acetate was treated with hydrogen sulphide for the removal of the excess of lead, and the filtered liquid concentrated under diminished pressure to the consistency of a syrup. This readily reduced Fehling's solution, and yielded *d*-phenylglucosazone, melting at 205—206°. In order definitely to establish the presence of dextrose, a portion of the syrup was heated with acetic anhydride, when penta-acetyldextrose, melting at 130—131°, was obtained. Another portion of the syrup was heated with dilute sulphuric acid, and after this treatment a small amount of scopoletin was isolated, thus indicating the presence of a glucoside of the latter substance.

Examination of the Resin (B).

The crude resin which had been separated from the aqueous liquid (A), as previously described, formed a dark brown mass, which when dry could be reduced to a light brown powder, and when treated with a little animal charcoal was obtained nearly colourless. After drying in a vacuum over sulphuric acid, it melted at 125—130°.

Optical Rotation of the Crude Resin.—For this determination a portion of the resin which had been obtained by the previously described assay of the root was first employed, its solution being deprived of colour by heating with a little animal charcoal (compare this vol., p. 8). A solution in absolute alcohol, of which 5 c.c. contained 0·3062 gram of resin, gave α_D $-1°13'$ in a 1-dcm. tube, whence $[\alpha]_D$ $-19·87°$.

Another determination, with the use of a little of the above-described resin (B), gave the following result:

A solution in absolute alcohol, of which 5 c.c. contained 0·4660 gram of resin, gave α_D $-1°53'$ in a 1-dcm. tube, whence $[\alpha]_D$ $-20·20°$.

Preliminary Extraction of the Crude Resin with Different Solvents.—In order to ascertain the general characters of the crude resin, a small portion (10 grams) of it was dissolved in alcohol, mixed with purified sawdust, and the thoroughly dried mixture extracted successively in a Soxhlet apparatus with various solvents. The amounts of extract, dried at 100°, were as follows:

Petroleum (b. p. 40—60°)	extracted	4·5	per cent.
Ether	,,	92·5	,, ,,
Chloroform	,,	0·4	,, ,,
Alcohol	,,	1·8	,, ,,
	Loss	0·8	,, ,,
		100·0	per cent.

For the purpose of a complete examination, the total amount of resin (866 grams) obtained by the above-described operation was employed. It was dissolved in alcohol, mixed with purified sawdust, and the thoroughly dried mixture extracted successively in a large Soxhlet apparatus with petroleum (b. p. 40—60°), ether, chloroform, ethyl acetate, and alcohol.

I. *Petroleum Extract of the Resin.*

This extract, after the removal of the solvent, was a dark brown, soft solid, amounting to 40 grams. It was dissolved in ether, and the ethereal solution extracted successively with aqueous ammonium carbonate and sodium carbonate, but only a trace of fatty material was removed by the latter solvent. The ether was then evaporated, and the residue heated for some time in a reflux apparatus with an alcoholic solution of potassium hydroxide, after which the mixture was diluted with water, and the alcohol removed in a current of steam. The alkaline liquid was then thoroughly extracted with ether, the ethereal liquid being washed, dried, and the solvent removed, when a quantity (4·5 grams) of a dark-coloured, crystalline product was obtained.

Isolation of a Phytosterol, $C_{27}H_{46}O$.

The above-mentioned crystalline product was recrystallised from a mixture of ethyl acetate and dilute alcohol, when it separated in pearly leaflets melting at 135—136°, which gave the colour reaction of the phytosterols:

0·7296, on heating at 110°, lost 0·0316 H_2O. $H_2O = 4·3$.

0·1114* gave 0·3418 CO_2 and 0·1238 H_2O. $C = 83·7$; $H = 12·3$.

$C_{27}H_{46}O,H_2O$ requires $H_2O = 4·5$ per cent.

$C_{27}H_{46}O$ requires $C = 83·9$; $H = 11·9$ per cent.

A determination of the specific rotatory power gave the following result:

0·5146,* made up to 20 c.c. with chloroform, gave α_D $-1°33'$ in a 2-dcm. tube, whence $[\alpha]_D$ $-30·1°$

The above-described substance was thus shown to be a phytosterol, and its identity was further confirmed by the preparation of an acetyl derivative, which separated from ethyl acetate in flat needles melting at 122—123°.

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* Anhydrous substance.

The alkaline liquid, from which the phytosterol had been removed by extraction with ether, was acidified, and again extracted with ether. This ethereal liquid was first shaken with a solution of ammonium carbonate, which, however, removed nothing. It was then shaken with aqueous sodium carbonate, which removed a quantity of fatty acids, and on finally evaporating the ether only a trace of amorphous material remained.

Identification of the Fatty Acids.

The sodium carbonate liquid obtained as above described was acidified and extracted with ether, the ethereal liquid being dried and the solvent removed. An oily product was thus obtained, which consisted of a mixture of acids. These were separated into liquid and solid portions by means of their lead salts.

The Liquid Acids.—When distilled under diminished pressure, these acids passed over between 220° and 240°/15 mm. as a pale yellow oil, and amounted to 9 grams. An analysis and a determination of the iodine value gave the following results:

0·1684 gave 0·4746 CO_2 and 0·1750 H_2O. C=76·9; H=11·5.

0·3322 absorbed 0·6355 iodine. Iodine value=191·3.

$C_{18}H_{34}O_2$ requires C=76·6; H=12·1 per cent. Iodine value=90·1.
$C_{18}H_{32}O_2$ „ C=77·1; H=11·4 „ „ Iodine value=181·4.
$C_{18}H_{30}O_2$ „ C=77·7; H=10·8 „ „ Iodine value=274·0.

The above results would thus indicate that the liquid acids consisted of a mixture of oleic, linolic, and linolenic acids.

The Solid Acids.—These acids, when recrystallised from ethyl acetate, melted at 55—57°, and amounted to 5 grams:

0·1476 gave 0·4102 CO_2 and 0·1690 H_2O. C=75·8; H=12·7.

0·1758 neutralised 0·0359 KOH. Neutralisation value=204.

$C_{16}H_{32}O_2$ requires C=75·0; H=12·5 per cent. Neutralisation value=219·1.

$C_{18}H_{36}O_2$ requires C=76·1; H=12·7 per cent. Neutralisation value=197·5.

It would thus appear that the solid acids consisted of a mixture of palmitic and stearic acids, the latter predominating.

II. *Ethereal Extract of the Resin.*

This extract, after the removal of the solvent, was a dark brown mass, which could easily be reduced to a light brown powder, and was stable in the air. It amounted to 800 grams. After treatment with a little animal charcoal it was obtained nearly colourless, and its optical rotatory power was then determined, with the following result: A solution in absolute alcohol, of which 5 c.c.

contained 0·3536 gram of the resin, gave α_D −1°21′ in a 1-dcm. tube, whence $[\alpha]_D$ −19·1°.

Hydrolysis of the Ethereal Extract with Barium Hydroxide.

A quantity (500 grams) of the dry ethereal extract of the resin was dissolved in alcohol, and, after the addition of a little water, a cold saturated solution of barium hydroxide was gradually added until the liquid showed an alkaline reaction. It was then kept at a temperature of 35—45°, and the alkalinity maintained by the further occasional addition of small portions of solution of barium hydroxide. This treatment was continued until the liquid gave no turbidity when mixed with water, after which the alcohol was removed by distillation in a current of steam, and a dark brown precipitate which had formed was collected.

Isolation of Ipuranol, $C_{23}H_{38}O_2(OH)_2$.

The above-mentioned dark brown precipitate amounted to 30 grams, and consisted for the most part of a barium compound. It was treated with acetic acid, when a small portion remained undissolved, and this, after being dried, was crystallised from a mixture of pyridine and ethyl acetate. The substance then separated in colourless, microscopic needles, melting at 285—290°, and was identified as ipuranol. (Found, C = 72·2; H = 10·6. Calc., C = 72·6; H = 10·5 per cent.) When heated with acetic anhydride the substance yielded diacetylipuranol, which, after crystallisation from ethyl acetate, melted at 162°.

The liquid from which the above-mentioned dark brown precipitate had separated was treated with carbon dioxide for the removal of the excess of barium, and, after filtration, dilute sulphuric acid was added until a precipitate just ceased to be produced, any excess of the mineral acid being carefully avoided. The liquid was again filtered, and then distilled in a current of steam until volatile acids ceased to pass over.

Isolation of d-*α-Methylbutyric and Tiglic Acids.*

The above-mentioned distillate, which amounted to about 6 litres, was neutralised with sodium carbonate, and concentrated to a small volume, then acidified, and extracted with ether. The ethereal liquid was dried, and the solvent removed, when a quantity (50 grams) of a colourless liquid was obtained, which was distilled under the ordinary pressure. The main portion passed over between 160° and 200°, whilst the last fraction (1·5 grams), which was unsaturated, became solid on cooling. In order to remove the small amount of unsaturated acid contained in the principal portion, the latter was treated with potassium permanganate in alkaline solution at 0°. On subsequently recovering the unchanged acid it was found to distil at 172—175°, and to possess the odour of a valeric acid. (Found, C=58·4; H=9·8. Calc., C=58·8; H=9·8 per cent.)

The density of the acid was 0·9356 at 24°, and a determination of its specific rotatory power gave, in a 50 mm. tube at 24°, $\alpha_D + 8°33'$, whence $[\alpha]_D + 18·2°$.

It was evident from these results that the above-described liquid consisted of *d*-α-methylbutyric acid.

The solid contained in the last fraction of the volatile acids was recrystallised from water, when it separated in flat needles melting at 64—65°, and was identified as tiglic acid. (Found, C=59·9; H=8·3. Calc., C=60·0; H=8·0 per cent.)

The aqueous liquid, from which the above-described acids had been extracted with ether, was distilled in a current of steam, when the distillate was found to contain very small amounts of formic and valeric acids.

Non-volatile Products of the Alkaline Hydrolysis.—After the removal of the *d*-α-methylbutyric and tiglic acids by distillation with steam, as above described, there remained in the distillation flask a dark yellow liquid, which was concentrated under diminished pressure to the consistency of a viscid syrup. This product amounted to 335 grams. When further dried, it could be reduced to a light brown powder, which, however, became glutinous on exposure to the air. It was freely soluble in water, and did not reduce Fehling's solution until after boiling with a dilute mineral acid.

The entire amount of the above-mentioned syrupy product was dissolved in alcohol, mixed with purified sawdust, and the thoroughly dried mixture extracted successively in a Soxhlet apparatus with ether, chloroform, ethyl acetate, and alcohol.

Ether and Chloroform Extracts of the Hydrolysed Resin (II).

These extracts were dark-coloured, viscid masses, amounting to 62 and 25 grams respectively. They were only sparingly soluble in water, and after heating with a 5 per cent. solution of sulphuric acid in aqueous alcohol yielded but small quantities of methyl jalapinolate (m. p. 47—49°) and jalapinolic acid (m. p. 67—68°), together with traces of formic and valeric acids. The liquids obtained by this treatment reduced Fehling's solution, but no osazone could be prepared from them.

Ethyl Acetate Extract of the Hydrolysed Resin (II).

This extract was a viscid mass, and amounted to 18 grams. When thoroughly dried it could be reduced to a light brown powder, which soon became glutinous on exposure to the air, but was only sparingly soluble in water. When heated with a 5 per cent. solution of sulphuric acid in aqueous alcohol, a little methyl jalapinolate was obtained, together with small amounts of jalapinolic, formic, and valeric acids. After the removal of the sulphuric acid from the remaining aqueous liquid, it reduced Fehling's solution and yielded *d*-phenylglucosazone (m. p. 205—206°), together with a small amount of an osazone melting at 180—182°. The latter was identical with an osazone of the same melting point prepared from the below-mentioned alcohol extract of the hydrolysed resin after treatment with dilute sulphuric acid, and was evidently rhamnosazone.

Alcohol Extract of the Hydrolysed Resin (II).

This represented the chief portion of the hydrolysed ethereal extract of the resin, and amounted to 230 grams. It was a light-coloured, amorphous mass, which could easily be powdered, and was stable in the air. It was readily soluble in water and in alcohol, and did not reduce Fehling's solution until after heating with a mineral acid. The aqueous solution was optically active, and a determination of the specific rotatory power gave the following result:

An aqueous solution, of which 5 c.c. contained 0·4798 gram of the extract, dried at 110°, gave α_D $-5°30'$ in a 2-dcm. tube, whence $[\alpha]_D$ $-28·6°$.

A quantity (150 grams) of the above-described product was dissolved in water, and such an amount of sulphuric acid added that the solution (1500 grams) contained 5 per cent. of its weight of acid. After heating the liquid for about three hours in a reflux apparatus, it was distilled in a current of steam until volatile products ceased to pass over. The distillate was then extracted with ether, the ethereal liquid being dried, and the solvent removed. A small quantity of liquid acid, distilling between 172° and 175°, was thus obtained, which was identified by means of its silver salt as a valeric acid. (Found, Ag=51·4. Calc., Ag=51·7 per cent.) The aqueous liquid from which the valeric acid had been removed was found to contain a small amount of formic acid.

After the removal of the volatile acids as above described, the distillation flask contained a dark yellow liquid with a cake of solid material floating on the surface. The whole was extracted with ether, which dissolved the solid substance, and the ethereal liquid was then shaken with aqueous sodium carbonate. On finally evaporating the ether, a small amount of a neutral substance was obtained, which separated from ethyl acetate in leaflets melting at 47—49°, and was evidently methyl jalapinolate.

Isolation of Jalapinolic Acid, $C_{15}H_{30}(OH)\cdot CO_2H$.

(*Hydroxyhexadecylic Acid.*)

The sodium carbonate extract of the above-mentioned ethereal liquid, which was almost solid, was treated with dilute sulphuric acid, and the liberated organic acid dissolved in ether. On removing the solvent, a quantity (30 grams) of an oily product was obtained, which solidified to a crystalline mass. This was recrystallised from dilute acetic acid, when a substance separated in small needles melting at 67—68°, which was identified as jalapinolic acid, $C_{16}H_{32}O_3$.* (Found, C=70·3; H=11·8. Calc., C=70·6; H=11·7 per cent.)

A portion of the acid was converted into its methyl ester, which, when recrystallised from ethyl acetate, separated in leaflets melting at 47—49°. (Found, C=71·0; H=11·9. Calc., C=71·3; H=11·9 per cent.)

The optical rotatory power of the ester was determined, with the following result:

3·7256, made up to 20 c.c. with chloroform, gave α_D +0°21′ in a 2-dcm. tube, whence $[\alpha]_D$ +0·94°.

The yellow, aqueous liquid, which had been extracted with ether as above described, was treated with barium hydroxide for the removal of the sulphuric acid, and, after filtration, concentrated under diminished pressure. A portion of the resulting syrup was treated with phenylhydrazine acetate, and the product examined according to the method described by A. G. Perkin (Trans., 1910, **97**, 1777), when two osazones were obtained. The chief portion of the product melted at 205—206°, and was evidently *d*-phenylglucosazone, whilst a small amount of a compound was separated which melted at 180—182°, and agreed in its characters with rhamnosazone. Another portion of the syrup was heated with acetic anhydride, when from the resulting product there was obtained a small quantity of penta-acetyldextrose, which separated from dilute alcohol in needles melting at 129—130°. No crystalline acetyl derivative of a methylpentose could be isolated, such as has been described by the authors in connexion with products obtained from the ethereal extract of the resin of *Ipomoea orizabensis* (this vol., p. 17), thus affording evidence that the latter differs appreciably in character from the corresponding resin of scammony root.

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* The so-called "scammonolic acid" of previous investigators, to which the formula $C_{16}H_{30}O_3$ was assigned, is identical with jalapinolic acid.

As the hydrolysed ethereal extract of the original resin evidently consisted in part of derivatives of both methyl jalapinolate and jalapinolic acid, it was deemed of interest to ascertain the relative proportions in which they were present. For this purpose a small quantity (5 grams) of the above-described alcoholic extract of the hydrolysed resin was acetylated by means of acetic anhydride in the presence of a trace of pyridine, the product dissolved in ether, and the ethereal liquid shaken with aqueous potassium hydroxide. By this means 2·5 grams of acidic material were removed, and on subsequently evaporating the ether 4·7 grams of a neutral product were obtained. Both these products on heating with dilute sulphuric acid yielded jalapinolic acid and a mixture of sugars, the neutral acetyl derivative also yielding a small amount (0·1 gram) of methyl jalapinolate.

III., IV., *and* V. *Chloroform, Ethyl Acetate, and Alcohol Extracts of the Resin.*

These extracts were dark-coloured, amorphous products, amounting to 2·6, 2·8, and 3·4 grams respectively. They were examined, but nothing definite could be isolated from them.

II.—*Examination of Scammony.*

For the purpose of comparing the previously described resin from scammony root with that obtained from the gum-resin known as scammony, a quantity of the latter was procured directly from Smyrna. The material possessed the general characters ascribed to an authentic product, although on incineration it yielded 3·52 per cent. of ash, which is slightly in excess of the pharmacopœial limits (compare, however, Guiques, *Bull. sci. pharmacol.*, 1909, **16**, 448, and Goris and Fluteaux, *ibid.*, 1910, **17**, 15). No starch or sugar was present.

A determination of the total resin was made by extracting 50 grams of the powdered material with alcohol in a Soxhlet apparatus, and mixing the concentrated alcoholic liquid with water, the precipitated resin being then thoroughly washed, and dried in a water-oven until of constant weight. The amount of resin obtained was 41·55 grams, being thus equivalent to 83·1 per cent. of the weight of scammony employed. It was completely soluble in ether. Neither the portion of the scammony which was insoluble in alcohol, nor the aqueous liquid obtained by the precipitation of the resin appeared to contain any substance of interest.

The optical rotatory power of the resin was determined with a small portion which had been decolorised by treatment with animal charcoal.

A solution in absolute alcohol, of which 5 c.c. contained 0·5042 gram of the resin, gave $\alpha_D -2°8'$ in a 1-dcm. tube, whence $[\alpha]_D -21·15°$.

Thirty grams of the resin were dissolved in alcohol, mixed with purified sawdust, and the thoroughly dried mixture extracted successively in a Soxhlet apparatus with light petroleum (b. p. 40—60°) and ether. The petroleum removed only 0·1 gram of soft, amorphous material, whereas the remainder of the resin, which was extracted by the ether, could easily be reduced to a powder, and after treatment with animal charcoal was obtained nearly colourless.

A solution in absolute alcohol, of which 5 c.c. contained 0·4384 gram of the purified ethereal extract of the resin, gave $\alpha_D -1°56'$ in a 1-dcm. tube, whence $[\alpha]_D -22·03°$.

For the further examination of the ethereal extract of the resin a small quantity (25 grams) was hydrolysed with a solution of barium hydroxide in the manner described in connexion with the corresponding extract of the resin from scammony root. The volatile acids (3·2 grams) obtained by this treatment consisted of a mixture of tiglic acid (m. p. 64°) and a valeric acid (b. p. 172—175°), the former being present in predominating amount.

After the removal of the above-mentioned volatile acids by distillation in a current of steam, there remained a dark yellow, strongly acid liquid, which was concentrated under diminished pressure to the consistency of a syrup. The latter was dissolved in alcohol, mixed with purified sawdust, and the thoroughly dried mixture extracted successively in a Soxhlet apparatus with ether, chloroform, ethyl acetate, and alcohol. The first three solvents removed 1·9, 0·85, and 0·3 gram respectively of amorphous, syrupy products, which were glucosidic in character, but the amounts did not permit of their further examination. The alcohol, on the other hand, removed 10·2 grams of an amorphous product, which, when dried, could be reduced to a powder, and was stable in the air. It was optically active.

An aqueous solution, of which 5 c.c. contained 0·2624 gram of the above product, gave $\alpha_D -3°6'$ in a 2-dcm. tube, whence $[\alpha]_D -29·5°$.

In order to ascertain the nature of the above-mentioned alcohol extract of the hydrolysed resin, a quantity (8 grams) was acetylated by means of acetic anhydride. The resulting product was poured into water, the precipitated compound dissolved in ether, and the ethereal liquid extracted with a solution of potassium hydroxide. On subsequently drying the ethereal liquid and evaporating the solvent, there remained about 7 grams of a light-coloured, amorphous mass. The alkaline liquid, when acidified and extracted with ether, yielded 2 grams of an amorphous, acidic product, thus showing that the hydrolysed resin was, for the most part, neutral in character. The above-mentioned neutral portion (7 grams) of the acetylated product, when heated with dilute sulphuric acid, gave small amounts of jalapinolic acid (m. p. 67—68°) and methyl jalapinolate (m. p. 47°), together with a sugar from which a little *d*-phenylglucosazone (m. p. 205—206°) was prepared.

Conclusions.

From the results of the preceding investigation it will be seen that the resins obtained from scammony root and from the gum-resin known as scammony, although similar in their general characters, are not perfectly identical. On the other hand, a comparison of the resin from scammony root with that obtained from the root of *Ipomoea orizabensis* (this vol., p. 1) shows that these two products differ very considerably in their composition. Both of these resins are exceedingly complex in character, but consist to a large extent of the glucosides and methylpentosides of jalapinolic acid, $C_{15}H_{30}(OH)CO_2H$, and its methyl ester. Whilst, however, the methylpentose obtained by the hydrolysis of the resin from scammony root appears to be identical with rhamnose, that from the resin of *Ipomoea orizabensis* (*loc. cit.*, p. 17) yields a crystalline tetra-acetyl derivative, which had not heretofore been described. The resin from the last-mentioned source contained, among other substances, small amounts of hentriacontane, $C_{31}H_{64}$, and cetyl alcohol, $C_{16}H_{34}O$, which were not present in the resin from scammony root, and, furthermore, very marked differences were observed in extracting both the crude resins and the products of their alkaline hydrolysis with various solvents. It is not to be expected, however, that products of this nature would be uniform in composition, and the differences which have now been observed to exist between them may not be constant, or such as appreciably to influence their therapeutic value.

In view of the complexity of the above-mentioned resins, it is evident that they cannot be represented by chemical formulæ, a fact which we had previously indicated in connexion with the investigation of jalap resin (*J. Amer. Chem. Soc.*, 1910, **32**, 112).

The names by which the resins now under consideration have heretofore been designated, such as "jalapin" or "scammonin," with the assumption that they were individual substances, should, therefore, also be discarded.

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L.—*The Hydrolysis and Saponification of Esters of Saturated and Unsaturated Acids.*

By THOMAS WILLIAMS and JOHN JOSEPH SUDBOROUGH.

As the result of numerous experiments it has been proved (Trans., 1898, **73**, 81; 1905, **87**, 1840; 1907, **91**, 1633; 1909, **95**, 315, 975) that the presence of an olefine linking in the $\alpha\beta$-position with respect to a carboxylic group has a most pronounced retarding effect on the rate of esterification of an organic acid when the catalytic method is employed. The effect is so marked that a mixture of an $\alpha\beta$-unsaturated acid and its saturated analogue can be readily separated by the method of fractional esterification (Sudborough and Thomas, Trans., 1911, **99**, 2307). Further experiments on the direct esterification of such acids (this vol., p. 237) prove that in the absence of a catalyst the difference in the rates of esterification is not nearly so marked. When, for example, the two acids have much the same dissociation constants, the relative rates of esterification of a saturated acid and the corresponding $\alpha\beta$-unsaturated acid are as 40:1 when the catalytic method is used, but only 4:1 or 5:1 in the absence of the catalyst. Using the direct method, it has been shown that when the unsaturated acid is much stronger than its saturated analogue it can be esterified more rapidly than the saturated acid, for example, methyl hydrogen maleate and methyl hydrogen succinate.

Some years ago (*Ber.*, 1895, **28**, 1263) V. Meyer put forward the generalisation that esters which are difficult to prepare are not readily hydrolysed. Such a broad generalisation cannot hold good, as esters are formed at very different rates, according to the method of esterification used, and, further, the esters are hydrolysed quite differently by different methods. Ethyl chloro- and dichloro-acetates are hydrolysed by dilute hydrochloric acid less readily than ethyl acetate (Kistiakowsky, *Zeitsch. physikal. Chem.*, 1898, **27**, 250), but are saponified by alcoholic potassium hydroxide solution much more readily than the unsubstituted ester (Sudborough and Feilmann, Proc., 1897, **13**, 241).

One of us has drawn attention to the resemblance between esterification by the direct method and hydrolysis of esters by means of water or alkalis, and on the other hand the resemblance between catalytic esterification and hydrolysis by means of dilute acids (see article "Hydrolysis" in Thorpe's Dictionary of Applied Chemistry, new edition).

We have studied the hydrolysis of the three following pairs of saturated and unsaturated esters: (1) Ethyl propionate and ethyl acrylate, (2) ethyl *n*-butyrate and ethyl crotonate, (3) ethyl β-phenylpropionate and ethyl cinnamate. The relative rates of hydrolysis by means of dilute hydrochloric acid and of saponification by means of dilute barium hydroxide have been determined at 20°. The hydrolysis by dilute hydrochloric acid is a unimolecular reaction, and the constants have been calculated by using the ordinary equation for such a reaction. Both ethyl cinnamate and ethyl β-phenylpropionate were dissolved in a mixture of alcohol and water, as they were not sufficiently soluble in water. Under these conditions an equilibrium was reached in the case of ethyl β-phenylpropionate, and the equation $K = 1/t \,.\, e/a \,.\, \log e/e - x$ was used for calculating K. K, x, and a have the usual meanings, and e is the equilibrium point expressed in c.c. of standard barium hydroxide. The experimental method adopted was as follows: For the acid hydrolysis a roughly 0·05N-solution of the ester was mixed with an equal volume of 0·05N-hydrochloric acid at 20°. The concentration of the hydrochloric acid in the mixture was determined immediately after mixing by titration with standard barium hydroxide, and the concentration of the ester determined by adding an excess of barium hydroxide to the neutralised solution, allowing to remain for several hours in a closed vessel, and titrating the excess of barium hydroxide by means of standard hydrochloric acid. For the alkali hydrolysis a 0·05N-aqueous solution of the ester (except in the case of cinnamic and β-phenylpropionic esters) was mixed at 20° with an approximately equivalent solution of barium hydroxide, and a portion of the mixture removed from time to time and titrated with standard hydrochloric acid. The concentration of the ester at the beginning was determined by adding an excess of barium hydroxide, keeping until hydrolysis was complete, and titrating the excess of alkali with standard acid. With ethyl cinnamate and ethyl β-phenylpropionate, 0·04N-solutions of ester and of barium hydroxide in 50 per cent. alcohol were used.

The esters used had the following boiling points: ethyl propionate, 98·3°; ethyl acrylate, 101—102°/765 mm.; ethyl butyrate, 120—121°/762 mm.; ethyl crotonate, 136—137°/762 mm.; ethyl β-phenylpropionate, 243—245°/767·5 mm.; and ethyl cinnamate, 272·6—272·8°/767·5 mm.

The results obtained are given in the following tables:

A. *Hydrolysis with Dilute Hydrochloric Acid.*

Concentration of barium hydroxide = 0·0418N.

Ester.	Concentration of HCl.	Time in hours, t.	Titration, $b+x$.	$a-x$.	$1/t \log a/a-x$.
Ethyl propionate ...	0·0495N	0	23·70	11·18	—
	b = 23·70	24	26·83	8·05	0·00593
		48	29·00	5·88	0·00581
		72	20·63	4·25	0·00583
		101	32·05	2·83	0·00591
		125	32·90	1·98	0·00600
	b = 23·70	0	23·70	11·03	—
		17	26·03	8·70	0·00606
		41	28·38	6·35	0·00584
		65	30·08	4·65	0·00577
		89	31·35	3·38	0·00577
		117	32·40	2·33	0·00577
		161	33·50	1·23	0·00591
Ethyl acrylate	0·04995N	0	23·90	10·80	—
	b = 23·90	113	24·50	10·20	0·000219
		255	25·20	9·50	0·000218
		354	25·60	9·10	0·000210
		656	26·70	8·00	0·000199
		896	27·60	7·10	0·000203
		1203	28·65	6·05	0·000210
	0·0496N	0	23·75	10·70	—
	b = 23·75	162	24·70	9·80	0·000235
		402	25·55	8·90	0·000199
		570	26·30	8·15	0·000207
		738	26·90	7·55	0·000205
		938	27·40	7·05	0·000193
		1098	27·75	6·70	0·000185
Ethyl butyrate	0·04995N	0	23·9	11·35	—
	b = 23·90	24	25·75	9·50	0·00322
		49	27·43	7·80	0·00332
		76	28·95	6·30	0·00336
		98	29·98	5·30	0·00337
		146	31·70	3·55	0·00346
		192	32·90	2·35	0·00355
	0·0495N	0	23·70	11·85	—
	b = 25·7	25·75	25·70	9·85	0·00308
		65	28·27	7·28	0·00326
		88	29·35	6·20	0·00320
		137·25	31·22	4·33	0·00318
		165·75	31·97	3·58	0·00318
		209·25	32·85	2·70	0·00307
Ethyl crotonate......	0·04995N	0	23·9	11·16	—
	b = 23·9	168	24·52	10·54	0·000145
		336	24·88	10·18	0·000119
		508·5	25·14	9·92	0·000105
		671	25·48	9·58	0·000099
		844	25·78	9·28	0·000095
		1056	26·13	8·93	0·000092
		1224	26·68	8·40	0·000102
		1392	26·82	8·25	0·000094

Ester.	Concentration of HCl.	Time in hours, t.	Titration, $b+x$.	$a-x$.	$1/t\log a/a-x$.
Ethyl crotonate......	0·497N	0	127·75	6·33	—
	$b=127·75$	72	128·80	5·28	0·00110
		144	129·80	4·28	0·00118
		240	130·80	3·28	0·00119
		408	132·05	2·03	0·00121
	$b=127·55$	0	127·55	6·33	—
		72	128·68	5·20	0·00118
		144	129·50	4·38	0·00111
		265	130·65	3·23	0·00111
		312	130·95	2·93	0·00107
		432	132·00	1·88	0·00122
Ethyl cinnamate ...	0·508N	0	130·50	5·37	—
	$b=130·50$	120	130·97	4·88	0·000344
		216	131·30	4·57	0·000324
		284	131·70	4·17	0·000382
		431	132·15	3·72	0·000370
		677	132·90	2·97	0·000380
		1008	133·55	2·32	0·000361
	$b=130·30$	0	130·30	5·37	—
		120	130·77	4·90	0·000332
		216	131·10	4·57	0·000324
		384	131·40	4·27	0·000346
		431	131·75	3·92	0·000317
		725	132·65	3·02	0·000344
		1008	133·10	2·57	0·000317

Ester.	Concentration of hydrochloric acid.	t, in hours.	$b+x$.	$c-x$.	$K=1/t.\,c/a\,\log c/c-x$.
Ethyl β-phenylpropionate	0·0510N	0	24·40	4·23	—
	$b=24·40$	24	24·90	3·73	0·00100
		50·5	25·42	3·21	0·00104
		96	26·20	2·43	0·00109
		144	26·85	1·80	0·00113
		213	27·27	1·36	0·00101
		282	27·72	0·90	0·00105
	0·0511N	0	24·45	4·21	—
	$b=24·45$	28	25·00	3·66	0·00095
		50	25·42	3·24	0·00100
		90·75	26·05	2·60	0·00101
		163·5	26·90	1·76	0·00102
		306	27·80	0·86	0·00099

B. *Saponification with Dilute Barium Hydroxide Solution.*

Barium hydroxide solution = 0·02525N; hydrochloric acid = 0·02355N.

Ester.	t, in hours.	$a-x$.	$b-x$.	$K=\frac{1}{t(a-b)}\log\frac{b(a-x)}{a(b-x)}$
Ethyl propionate ...	0·0	19·80	21·45	—
	0·083	12·40	14·05	0·142
	0·25	7·30	8·95	0·130
	0·50	4·35	6·00	0·127
	0·75	3·00	4·65	0·125
	1·00	2·20	3·85	0·126
	0·0	19·80	21·45	—
	0·88	12·25	13·90	0·140
	0·254	7·25	8·90	0·130
	0·50	4·45	6·10	0·124
	0·75	3·15	4·80	0·120
	1·00	2·35	4·00	0·119

Ester.	t. in hours.	$a-x$.	$b-x$.	$K=\frac{1}{t(a-b)}\log\frac{b(a-x)}{a(b-x)}$.
Ethyl acrylate ……	0·0	19·15	21·45	—
	0·17	8·80	11·10	0·134
	0·33	5·40	7·70	0·137
	0·52	3·70	6·00	0·136
	0·77	2·40	4·70	0·138
	0·0	19·15	21·45	—
	0·083	12·00	14·30	0·140
	0·27	6·55	8·85	0·133
	0·52	3·70	6·00	0·136
	0·77	2·40	4·70	0·138
Ethyl butyrate……	0·0	19·75	20·85	— *
	0·083	14·90	16·00	0·0792
	0·267	9·79	10·89	0·0774
	0·55	6·35	7·45	0·0756
	1·15	3·52	4·62	0·0744
	0·0	19·75	20·85	—
	0·083	14·75	15·85	0·0756
	0·28	9·40	10·50	0·0786
	0·61	5·93	7·03	0·0750
	1·08	3·57	4·67	0·0780
Ethyl crotonate …	0·0	20·30	20·85	—
	0·28	15·45	16·00	0·0224
	0·60	12·70	13·25	0·0203
	1·57	8·17	8·72	0·0193
	2·62	5·70	6·25	0·0197
	0·0	20·30	20·85	—
	0·27	15·85	16·40	0·0205
	0·67	12·25	12·80	0·0199
	1·71	7·67	8·22	0·0194
	2·70	5·60	6·15	0·0194
Ethyl β-phenyl-propionate.	0·0	16·62	16·75	— †
	0·25	13·42	13·55	0·0246
	0·5	11·34	11·47	0·0231
	1·0	8·87	9·00	0·0223
	2·0	6·22	6·35	0·0215
	3·0	4·72	4·85	0·0215
	0·0	16·62	16·75	—
	0·25	13·62	13·75	0·0246
	0·5	11·47	11·60	0·0246
	1·0	8·87	9·00	0·0223
	2·0	6·17	6·30	0·0215
	4·0	3·52	3·65	0·0238
Ethyl cinnamate …	0·0	16·50	16·70	— ‡
	0·5	14·80	15·00	0·00600
	1·0	13·35	13·55	0·00600
	2·0	11·35	11·55	0·00600
	3·0	9·80	10·00	0·00600
	4·0	8·80	9·00	0·00564
	0·0	16·50	16·70	—
	0·5	14·75	14·95	0·00696
	1·0	13·45	13·65	0·00600
	2·0	11·35	11·55	0·00600
	3·0	9·95	10·15	0·00564
	4·0	8·85	9·05	0·00564

* $Ba(OH)_2=0·0249N$. $HCl=0·02387N$.

† $Ba(OH)_2=0·0200N$. $HCl=0·02387N$.

‡ $Ba(OH)_2=0·0197N$. $HCl=0·02355N$.

These numbers give the following values for the constants of hydrolysis, using *N*-hydrochloric acid:

Ethyl propionate	0·119
,, acrylate	0·00416
,, butyrate	0·0657
,, crotonate	0·00225
,, β-phenylpropionate	0·0201
,, cinnamate	0·000672

and the following comparative saponification values for standard barium hydroxide:

Ethyl propionate	5·44
,, acrylate	5·78
,, butyrate	3·213
,, crotonate	0·842
,, β-phenylpropionate	0·964
,, cinnamate	0·255

The numbers for ethyl β-phenylpropionate and ethyl cinnamate are not directly comparable with the values obtained for the other esters, as these esters were dissolved in a mixture of alcohol and water, and not simply in water.

The numbers at once indicate that in the case of the three pairs of compounds examined the ester of the saturated acid is hydrolysed by dilute hydrochloric acid about thirty times as readily as the corresponding unsaturated ester, but that when hydrolysed by dilute barium hydroxide the difference is not nearly so marked, the ratio of saponification of a saturated ester and its unsaturated analogue being about 4 to 1, except with ethyl propionate and ethyl acrylate, where the ratio is 1 : 1·1. This may be due in part to the fact that acrylic acid is a much stronger acid than propionic, the dissociation constants being respectively 0·0056 and 0·00134. The values for the dissociation constants of the other acids are: butyric, 0·00149; crotonic, 0·00204; β-phenylpropionic, 0·00227; and cinnamic, 0·00355.

These results indicate that the relationship between hydrolysis of esters by acids and catalytic esterification is marked, and also that between direct esterification of an acid and hydrolysis of the esters by alkalis.

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BANGALORE.

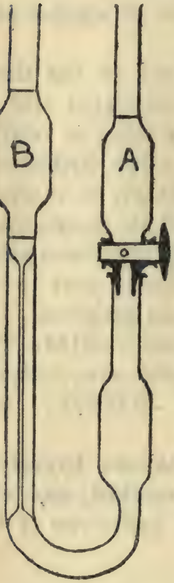
LI.—*The Viscometric Determination of Transition Points.**

By Albert Ernest Dunstan and Harold Langton.

In connexion with an investigation which the authors are conducting on the existence of double salt molecules in the dissolved state, a simple method has been developed for the determination of transition points.

In brief, this method consists in measuring and plotting the viscosities of saturated solutions of the various compounds at different temperatures, when a curve is obtained on which singular points are exhibited at the transition temperatures.

Fig. 1.



The solution to be examined was stirred at constant temperature for a prolonged time, varying from two to seven hours in the cases examined in this investigation. A viscometer was designed to allow of the saturated solution being filtered directly into the instrument, and incidentally to carry out a density determination to check the course of the saturation. To this end the measuring bulb *A* of the modified Ostwald viscometer described by one of the present authors (Trans., 1907, **91**, 1730) was ground into the receiving limb instead of being fused on (Fig. 1). To the tap could be attached a filtering tube of the usual type. When filled with the clear solution, this measuring bulb was supported in the thermostat, and the level of the liquid adjusted to the mark. Before filling, the bulb was warmed in the bath. On being dried and cooled, a density determination could be made, since the bulb was previously calibrated. Any solid that separated was soon redissolved when the bulb was immersed in warm water. It was then connected with the viscometer, the tap opened, and after a sufficient time for temperature equilibrium the liquid was sucked up above the mark in the delivery bulb *B*. A rapid method for the determination of the transition point is thus possible, the rapidity being only conditioned by the time required for saturation to be set up. In each of the series of experiments described below, analyses were made of the solid phase in equilibrium with the solution, and each experimental point is the mean of several determinations of times of flow. It will be seen from the curves that points on the metastable curves have been recorded on several occasions.

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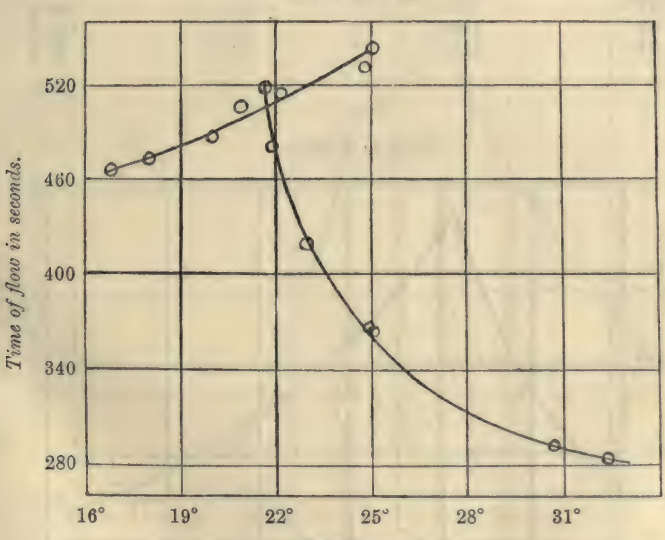
* For abstract, see Proc., 1912, **28**, 14.

Astrakanite.

This salt was prepared by dissolving molecular proportions of sodium and magnesium sulphates in as little water as possible, and evaporating the solution on the water-bath until on stirring a copious precipitate of the double salt occurred. This was collected, and dried on porous earthenware. Several analyses were made to find the percentage of water of crystallisation, which was found to be 21·53 (calculated for $Na_2SO_4,MgSO_4,4H_2O = 21{\cdot}60$). Some difficulty was met with in obtaining equilibrium, and prolonged stirring was needed. The transition temperature is 21·7°. The metastable curve for the mixed sulphates is well shown.

FIG. 2.

Astrakanite.



Temperature.

Temperature.	Time of flow (seconds).	Temperature.	Time of flow (seconds).
32·4	283·5	21·5	518·0
30·7	291·0	20·9	506·0
25·0	528·0	20·05	486·5
24·9	365·0	17·95	474·0
23·0	419·0	16·78	467·3
21·9	480·0		

Starting with the mixed sulphates at 25°, it was possible by varying the period of stirring to obtain values for the time of flow ranging between 540 and 360 seconds, depending on the degree of persistence of the metastable condition.

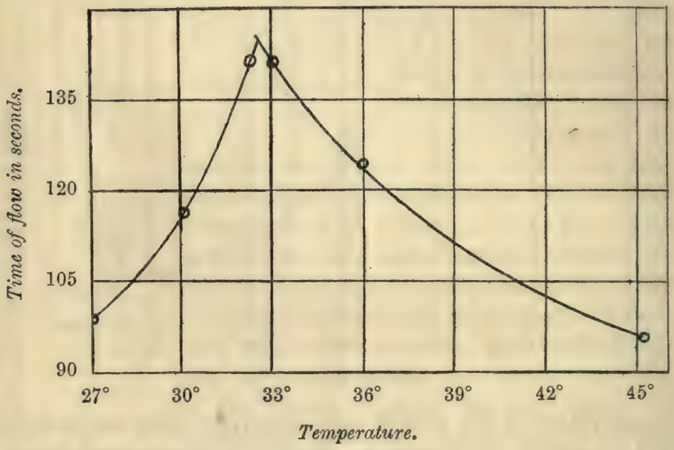
Sodium Sulphate, $Na_2SO_4,10H_2O$.

Recrystallised from Schuchardt's purest preparation. The anhydrous salt, Na_2SO_4, was prepared from this.

Temperature.	Time of flow (seconds).	Temperature.	Time of flow (seconds).
27·0	98·3	33·0	141·2
30·0	116·0	36·0	124·0
32·45	141·4	45·2	95·0

FIG. 3.

Sodium sulphate.



The transition point from the intersection of the curves for the anhydrous and decahydrated salts is 32·6°. Richards and Wells (*Zeitsch. physikal. Chem.*, 1903, **43**, 471) find 32·4°.

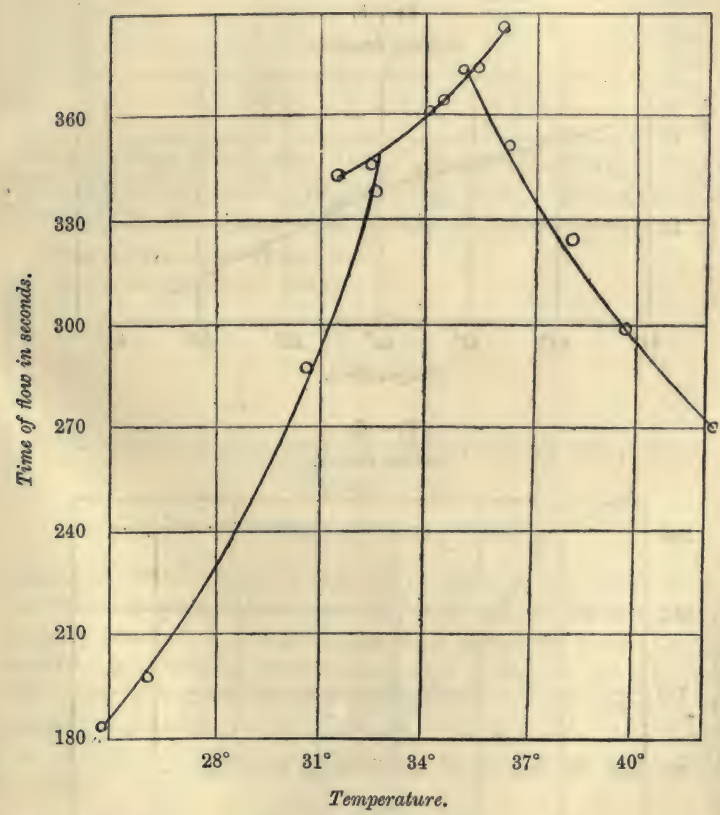
Sodium Carbonate.

The crystallised decahydrate used was Schuchardt's purest preparation. The monohydrate was obtained from the effloresced decahydrate.

Temperature.	Time of flow (seconds).
24·8	183·5
26·1	197·0
30·6	287·0
31·5	343·0
32·4	346·0
32·5	338·0
34·1	362·0
34·5	365·0
35·0	374·0
35·5	374·0
36·2	386·0
36·4	352·0
38·2	324·0
39·7	298·0
42·35	270·5

FIG. 4.

Sodium carbonate.



The transition point for $Na_2CO_3,10H_2O$—$Na_2CO_3,7H_2O$ is 32·5°, and for $Na_2CO_3,7H_2O$—Na_2CO_3,H_2O is 35·4°. Ketner (*Annalen*, 1872, **25**, 546) gives 31·85° and 35·1° respectively.

Sodium Bromide.

Recrystallised from Kahlbaum's purest dihydrated salt. The anhydrous phase was prepared from the crystalline dihydrate.

Temperature.	Time of flow (seconds).	Temperature.	Time of flow (seconds).
41·0	66·4	50·3	61·6
43·9	65·0	51·3	60·2
45·7	63·6	53·8	58·0
48·4	62·3	56·7	54·9
49·0	62·2		

FIG. 5.

Sodium bromide.

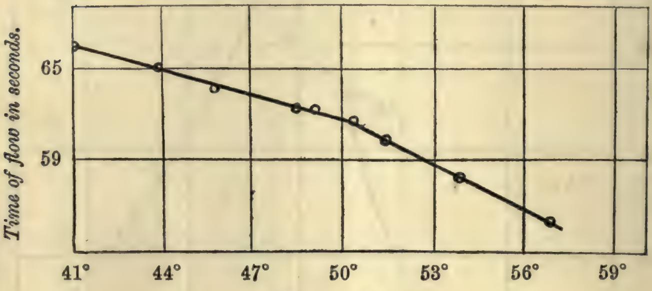
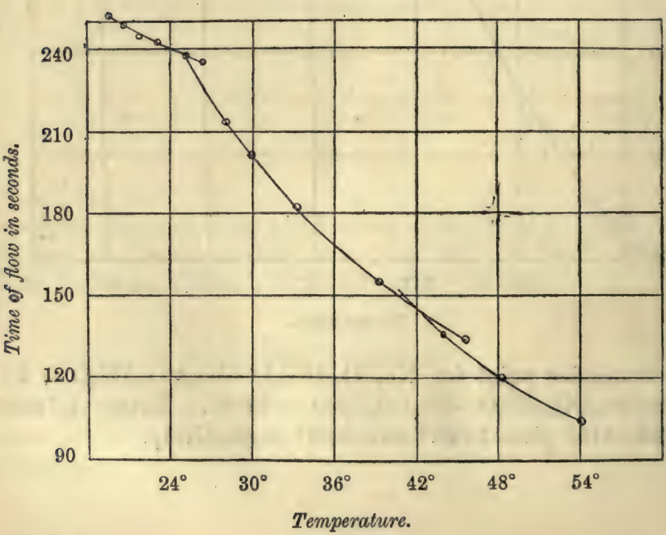


FIG. 6.

Barium acetate.



The transition point for NaBr,$2H_2O$—NaBr is at 50·5°. Richards and Churchill (*Zeitsch. physikal. Chem.*, 1899, **28**, 314) found 50·7°.

Barium Acetate.

The hydrate was crystallised from Schuchardt's preparation. The monohydrate was prepared by efflorescence of the trihydrate, and the anhydrous phase by heating the monohydrate in a steam-oven.

Temperature.	Time of flow (seconds).	Temperature.	Time of flow (seconds).
19·5	252·0	30·2	201·0
20·6	249·2	33·2	182·0
21·75	244·2	39·2	155·0
23·25	243·0	43·9	136·8
25·3	238·3	45·5	134·0
26·4	235·0	48·2	120·7
28·1	212·7	54·0	104·0

The transition points are: $Ba(C_2H_3O_2)_2,3H_2O$—$Ba(C_2H_3O_2)_2,H_2O$, 25·2°; $Ba(C_2H_3O_2)_2,H_2O$—$Ba(C_2H_3O_2)_2$, 42·2°. Walker and Fyffe (Trans., 1903, **83**, 173) find 24·7° and 41° respectively.

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LII.—*Hydroxymethylphosphinic Acid and Some Homologues.*

By HAROLD JAMES PAGE.

FOSSEK (*Monatsh.*, 1884, **5**, 121, 627; 1886, **7**, 20) found that the admixture of phosphorus trichloride (1 mol.) and an aldehyde (3 mols.) resulted in the formation of a viscid oil, with the liberation of a considerable quantity of heat. When the oil was treated with water, two-thirds of the initial quantity of aldehyde were regenerated, together with hydrogen chloride; and an acid of the type $R{\cdot}CH(OH){\cdot}PO_3H_2$ was formed according to the following equations:

$$3R{\cdot}CHO + PCl_3 = [3R{\cdot}CHO,PCl_3]$$

$$[3R{\cdot}CHO,PCl_3] + 3H_2O = 2R{\cdot}CHO + 3HCl + R{\cdot}CH(OH){\cdot}PO_3H_2.$$

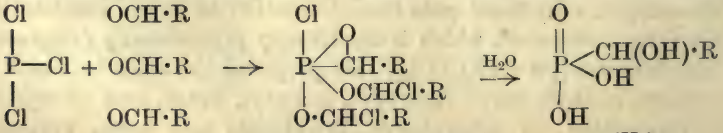
Fossek (*loc. cit.*) could gain no information as to the constitution of the intermediate oil, which is accordingly provisionally designated by the formula $[3R{\cdot}CHO,PCl_3]$. He prepared the acids in which R represents methyl, ethyl, *iso*propyl, *iso*butyl, hexyl, and phenyl by the interaction of phosphorus trichloride and acet-, propion-, *iso*butyr-, *iso*valer-, hept-, and benz-aldehydes respectively; moreover, he advanced conclusive evidence that their structure is as represented above.

The present communication deals with a repetition and extension of Fossek's investigations, and was undertaken for two reasons: first, on account of the exceedingly interesting nature of the reaction whereby the hydroxyphosphinic acids are produced; and secondly, because the first member of the series, hydroxymethylphosphinic acid, $OH\cdot CH_2\cdot PO_3H_2$, was not prepared by Fossek.

Fossek's results have been confirmed, but certain minor modifications in his methods have been of advantage; these are mentioned in the experimental part of this communication.

The intermediate oil is of an extremely unstable nature; an attempt to distil it in a vacuum resulted in its decomposition into aldehyde, hydrogen chloride, etc. There is, however, no doubt that it contains 3 molecules of aldehyde to 1 of phosphorus trichloride in chemical union, for if these two are mixed in any other proportions, the whole of the excess of one or the other above these proportions can be rapidly removed in a vacuum at the ordinary temperature. The regeneration of two of the three initial molecules of aldehyde by the action of water has also been amply confirmed. Any attempt at explaining the mechanism of the reaction and the constitution of the intermediate oil must take account of these facts; it must also explain the fact that, whereas at the commencement of the reaction the phosphorus is in the tervalent condition, in the final product, the hydroxyphosphinic acid, the phosphorus is quinquevalent. The above considerations have led the author tentatively to advance the following explanation of the mechanism of the reaction:

The phosphorus trichloride and aldehyde first combine to form an additive compound, in which the phosphorus is linked to each of the carbon atoms of the original aldehyde groups by the oxygen atoms of these groups. In view of the well-known tendency of phosphorus to pass from the tervalent to the quinquevalent condition wherever possible, the molecule of this compound undergoes a rearrangement to produce a compound of formula (I), in which the phosphorus has assumed the quinquevalent condition, and at the same time has become directly united to a carbon atom. The compound (I) when acted on by water is decomposed in such a way



(I.) (II.)

that the P·O·C linkings are hydrolysed, whereas the P·C linking is unchanged, and the hydroxyphosphinic acid (II) is formed. This explanation is in harmony with all the known facts of the reaction; and the instability of the intermediate oil, although it renders experimental proof well-nigh impossible, supports the constitution (I).

The obvious method of preparing hydroxymethylphosphinic acid would appear to be by the interaction of dry formaldehyde with phosphorus trichloride. Fossek (*loc. cit.*), however, had already found that in the case of acetaldehyde the reaction was so violent that his usual method had to be modified considerably. It was hence to be anticipated that the reaction with formaldehyde would be still more violent; and, moreover, the experimental difficulties are increased by the excessive tendency of dry formaldehyde to polymerise. A satisfactory method was finally found in the interaction of phosphorus trichloride with paraformaldehyde or trioxymethylene, the termolecular polymeride of formaldehyde. By this means ***hydroxymethylphosphinic acid,*** $OH\cdot CH_2\cdot PO_3H_2$, was obtained in 93 per cent. yield. At the same time, it was deemed advisable to attempt the preparation of this compound, for purposes of comparison, from formaldehyde and phosphorus trichloride; ultimately a method was devised whereby a small quantity of the desired product was obtained, not sufficiently pure for analysis, but its identity with the product from trioxymethylene was established.

Hydroxymethylphosphinic acid was found to be in most respects analogous to the other members of the series; being, however, the typical member, it was to be expected to show certain anomalous properties, and such was, in fact, found to be the case. Especially interesting is the property which it possesses of inhibiting the precipitation of phosphates by ammonium molybdate. It is also extraordinarily hygroscopic and deliquescent; moreover, it reduces ammoniacal silver nitrate readily at 100°. These properties are not found in the other members of the series. Some explanation is possibly to be found in the fact that it contains a primary alcoholic group, whereas the other members contain secondary alcoholic groups.

EXPERIMENTAL.

Preparation of α-Hydroxybenzylphosphinic Acid, $OH\cdot C_7H_6\cdot PO_3H_2$.

This compound was prepared by Fossek's (*loc. cit.*) original method. One hundred and fourteen grams of benzaldehyde were cautiously mixed with 37 grams of phosphorus trichloride, and set aside for twenty-four hours. A faintly red, fluorescent, viscid oil resulted, which was poured into 3 litres of cold water with constant stirring. The lower layer of benzaldehyde was separated, and shaken with successive quantities of water, which were added to the main aqueous portion. This was filtered through a wet filter paper to remove globules of benzaldehyde, and evaporated on the water-bath to a syrup, which was redissolved in water and re-evaporated several times in order to remove all traces of hydrochloric acid. Contrary to Fossek's statement, it was found that the syrup did not crystallise; on treatment with ether, however, it became beautifully crystalline without previously passing entirely into solution. These crystals were collected, and recrystallised from a mixture of two parts of benzene and one part of glacial acetic acid. The yield was 42 grams, that is, 84 per cent. of the theoretical. (Found, C=44·3*; H=4·9; P=16·5.† Calc., C=44·68; H=4·79; P=16·5 per cent.)

The α-hydroxybenzylphosphinic acid melted sharply at 211° (uncorr.). Fossek (*loc. cit.*) found 173°.

The *calcium* salt was prepared by adding calcium chloride to a neutral solution of the ammonium salt of the acid, and boiling; this precipitates the calcium salt, which is much less soluble at 100° than it is at the ordinary temperature. It was collected at 100°, and dried at 110°:

Found: P=13·3.

$C_7H_7O_4PCa$ requires P=13·7 per cent.

Investigation of the Oily Intermediate Compound.

Thirty-one grams (1 mol.) of phosphorus trichloride were mixed as before with 95·5 grams (4 mols.) of benzaldehyde. The mixture was set aside for twenty-four hours, and then kept in a vacuum until its weight was constant. It was then found to weigh 103 grams, which corresponds with the loss of 23·5 grams (1 mol.) of benzaldehyde. Fifty grams of this oil were poured into 1000 c.c. of water. The benzaldehyde liberated, together with that dissolved in the water, amounted to 48 grams, that is, two-thirds of the benzaldehyde in the intermediate oil had been regenerated. The remainder of the oil was fractionally distilled in a vacuum. Three main fractions were obtained, which were further divided into eight sub-fractions. These were all colourless and mobile, and had an odour resembling that of a mixture of benzaldehyde and hydrogen chloride. On keeping in air they were all completely converted into benzoic acid. They contained no phosphorus, and amounts of chlorine which increased from 3·6 per cent. in the first fraction to 27·64 per cent. in the eighth. These fractions were clearly either solutions of hydrogen chloride in benzaldehyde, or they contained some extremely unstable compound which readily gave these two substances.

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* In these combustions, the substance was mixed with lead chromate in the boat; otherwise a residue of phosphoric acid containing unburnt carbon was left.

† This, and all subsequent determinations of phosphorus, are carried out by Neumann's method, as modified by Plimmer and Bayliss (*J. Physiol.*, 1906, **33**, 439). The substance is oxidised with a mixture of nitric and sulphuric acids, diluted with water, and the phosphoric acid precipitated with ammonium molybdate under standard conditions. The precipitate is collected, washed, and dissolved in excess of standard sodium hydroxide; the excess of alkali is titrated with acid after boiling off all ammonia.

*Preparation of α-Hydroxy*iso*amylphosphinic Acid,* $OH\cdot C_5H_{10}\cdot PO_3H_2$.

This compound was prepared by Fossek's (*loc. cit.*) original method. Twenty-seven grams (4 mols.) of *iso*valeraldehyde were cautiously mixed with 11 grams (1 mol.) of phosphorus trichloride, and the mixture set aside for twenty-four hours. It was then poured into 750 c.c. of water, and thoroughly stirred. The upper layer of *iso*valeraldehyde was separated, and amounted to 18 grams. The aqueous layer was filtered through moist filter paper, and evaporated to a syrup on the water-bath, when on cooling it crystallised completely. It was recrystallised from a mixture of alcohol and ethyl acetate, and dried at 110°. When it was analysed, even after mixing intimately with lead chromate, it was found that it gave values for carbon which varied between 1 and 2 per cent. below the true value. (Found, C=33·6, 33·2, 34·0. Calc., C=35·7 per cent.)

Messinger's method, as modified by Fritsch (*Annalen*, 1897, **294**, 79), in which the carbon is estimated by oxidation with sulphuric acid and potassium dichromate, gave results even lower than this, namely, C=21·3 per cent.

Since Fossek (*loc. cit.*) obtained theoretical results for carbon, it is obvious that he must have used some modification of the ordinary method, which he does not mention. It is noticeable that the difficulty was not encountered with α-hydroxybenzylphosphinic acid. The results for hydrogen and phosphorus are, however, well in agreement with theory, and serve to make the identity of the compound assured. (Found, H=7·7; P=18·6. Calc., H=7·7; P=18·5 per cent.) The α-hydroxy*iso*amylphosphinic acid melted at 188° (uncorr.); Fossek's preparation melted at 184—185°.

Hydroxymethylphosphinic Acid, $OH{\cdot}CH_2{\cdot}PO_3H_2$.

Seventy-eight grams of trioxymethylene were added in successive small portions to 118 grams of phosphorus trichloride. Each addition of trioxymethylene caused the evolution of much heat, and the mixture was cooled thoroughly after each addition. A viscid mass, in appearance resembling starch paste, was produced. When this was heated on the water-bath for a few minutes it gradually became clear, and after an hour it was a fairly viscous oil. This was set aside for twenty-four hours, and then poured into 4000 c.c. of water. The oil first sank to the bottom, but gradually dissolved, with the evolution of a considerable quantity of formaldehyde. After the oil had completely disappeared, the aqueous liquid was filtered, and evaporated on the water-bath until of constant bulk. When set aside for twenty-four hours out of contact with air, the whole mass crystallised in long, flat prisms radiating from the point of contact of a glass rod with the basin. The mass was broken up, and separated so far as possible from the small quantity of viscid, oily liquid which it contained. When placed in a vacuum over concentrated sulphuric acid it was not observed to become any drier; indeed, it was found to be more hygroscopic than sulphuric acid. It could, however, be dried over phosphoric oxide. A second crop was obtained in a similar way from the mother liquor, the total yield being 90 grams, or 93 per cent. of the theoretical (for 1 mol. PCl_3 : 1 mol. CH_2O). The only effective method of recrystallisation was to dissolve in absolute alcohol, and add ethyl acetate until a permanent cloudiness was obtained. After some hours a mass of crystals (slender, rectangular prisms) was obtained. These were separated, and dried in a vacuum over phosphoric oxide, when they melted at 85° (uncorr.). The same difficulty with regard to combustions was met with as in the case of α-hydroxy*iso*amylphosphinic acid, even when the substance was intimately mixed with dry lead chromate (in absence of air, since the acid is very hygroscopic).

Found: $C = 9{\cdot}3,\ 9{\cdot}6$.

CH_5O_4P requires $C = 10{\cdot}7$ per cent.

Here, again, the Fritsch-Messinger wet method gave even more discordant results. (Found, $C = 5{\cdot}56,\ 5{\cdot}67$.)

The reasons for the non-applicability of any of the known methods of combustion to these compounds are not known, and the matter is being further investigated. The values for hydrogen and phosphorus, together with the analyses of various salts, were, however, sufficient proof of the identity of the substance with hydroxymethylphosphinic acid.

Found: H = 4·2, 4·1; P = 27·9, 27·5.

0·2290 gram lowered the freezing point of 23·31 grams of glacial acetic acid by 0·324°. M.W. = 118.

CH_5O_4P requires H = 4·5; P = 27·7 per cent. M.W. = 112.

This shows that the substance has the simple formula CH_5O_4P, and is hence a derivative of formaldehyde, not of trioxymethylene, which latter is hence depolymerised during its reaction with phosphorus trichloride.

Hydroxymethylphosphinic acid is a white solid, crystallising in rectangular platelets. It is exceedingly hygroscopic and deliquescent. It is a dibasic acid, as shown by the following titrations:

A solution of the acid was titrated with *N*/2-sodium hydroxide, using, first, phenolphthalein, and, secondly, alizarin-red as indicators.

Indicator.	Volume of acid solution.	Volume of *N*/2-NaOH.
Alizarin-red.............. ..	25 c.c.	6·95 c.c.
Phenolphthalein	25 ,,	13·90 ,,

It is not decomposed by boiling with dilute acid or alkali. When treated with potassium permanganate in acid solution it is entirely oxidised, the whole of the phosphorus being converted into phosphoric acid. It reduces ammoniacal silver nitrate solution rapidly on heating, but does not produce a mirror. It has no action on Fehling's solution. When heated alone it first melts, then evolves formaldehyde, leaving a residue of phosphorous acid, which on further heating evolves phosphine, leaving a residue of phosphoric acid.

The inhibitory action of hydroxymethylphosphinic acid on the precipitation of ammonium phosphomolybdate, although it itself forms no insoluble compound with the latter, is shown by the following experiment. Saturated sodium phosphate solution was added drop by drop to the contents of each of two test-tubes, the first of which contained 10 per cent. of ammonium molybdate in 2*N*-nitric acid, and the second contained 10 per cent. of ammonium molybdate and *N*/2-hydroxymethylphosphinic acid in 2*N*-nitric acid. Whereas the first drop of sodium phosphate produced a copious, yellow precipitate of ammonium phosphomolybdate in the first tube, no precipitate was produced in the second, even after the addition of fifteen drops, and it was only after several c.c. of sodium phosphate had been added that any phosphomolybdate was precipitated, and then only after some time. The nature of this inhibitory action is not yet understood.

Salts of Hydroxymethylphosphinic Acid.

The *barium* and *barium hydrogen* salts were prepared by the addition of the calculated quantity of barium hydroxide to a solution of the acid. The barium hydrogen salt is precipitated by alcohol, but not in a filterable form. When its solution is evaporated, crystals of the neutral salt separate, and free acid remains in the mother liquor.

Barium hydroxymethylphosphinate may be prepared as above, or by boiling its solution in water, when it is precipitated in pearly plates. It is less soluble in hot water than in cold.

Found: $P = 12{\cdot}6$.

CH_3O_4PBa requires $P = 12{\cdot}5$ per cent.

Silver hydroxymethylphosphinate is a white, amorphous substance. When heated to 100° it rapidly becomes black.

Found: $P = 9{\cdot}3$.

$CH_3O_4PAg_2$ requires $P = 9{\cdot}6$ per cent.

Pyridinium hydroxymethylphosphinate,

$$OH{\cdot}CH_2{\cdot}PO_3H_2,C_5H_5N,$$

is obtained in glistening, white needles by the addition of pyridine to a solution of hydroxymethylphosphinic acid in absolute alcohol. It melts at 105° (uncorr.). In similar concentrations, α-hydroxybenzyl- and α-hydroxy*iso*amyl-phosphinic acids do not form insoluble pyridinium salts. The salt readily loses pyridine.

Found: $P = 16{\cdot}7$.

CH_5O_4P,C_5H_5N requires $P = 16{\cdot}3$.

Calcium hydroxymethylphosphinate is a white, amorphous substance, much more soluble in cold water than in hot. The *calcium hydrogen* salt is an uncrystallisable syrup. The following salts are amorphous: the *lead* and *zinc* salts (colourless), the *cupric* salt (pale blue), and the *ferric* salt (pale yellow).

The *mercuric* and *magnesium* salts are soluble in water.

Action of Formaldehyde on Phosphorus Trichloride.

Dry formaldehyde generated by the action of heat on trioxymethylene was passed into thoroughly cooled phosphorus trichloride. A considerable quantity of heat was liberated. Long before the theoretical amount of formaldehyde had been passed in, the whole of the tubes were blocked by the polymerisation of the formaldehyde to trioxymethylene. The interesting point, however, was that the greater part of the formaldehyde coming into contact with the phosphorus trichloride had polymerised and produced a starch-paste-like mass similar to that produced in the preparation of hydroxymethylphosphinic acid. This mass was shown to contain trioxymethylene; it is hence evident that the action of phosphorus trichloride on formaldehyde is preceded by, or at any rate accompanied by, polymerisation of the formaldehyde. When the starch-paste-like mass was heated, it became clear, and although hydroxymethylphosphinic acid could not be isolated in the pure state from the liquid produced by treating with water, on account of the large amount of phosphorous and phosphoric acids present, a product was obtained which possessed all the properties of hydroxymethylphosphinic acid, including that of inhibiting the precipitation of phosphomolybdate.

The author wishes to express his thanks to Dr. R. H. Aders Plimmer for valuable advice, and to the Government Grant Committee of the Royal Society for a grant, which has partly defrayed the expenses of this investigation.

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LIII.—*An Exact Investigation of the Three Component System: Sodium Oxide, Acetic Anhydride, Water.*

By ALFRED CHARLES DUNNINGHAM.

THIS system has already been investigated at 30° by Dukelski (*Zeitsch. anorg. Chem.*, 1909, **62**, 114), who gave the following as the phases stable at that temperature: $C_2H_3O_2Na,\frac{1}{2}H_2O$; $C_2H_3O_2Na,3H_2O$; $C_2H_3O_2Na,C_2H_4O_2$; and $C_2H_3O_2Na,2C_2H_4O_2$.

The research described below was undertaken for the following reasons:

(1) It appeared improbable that a hydrated salt should exist at 30° in contact with a concentrated solution of sodium hydroxide, especially as anhydrous sodium acetate is not deliquescent. According to Dukelski, however, the hemihydrate can exist in contact with a saturated solution of sodium hydroxide.

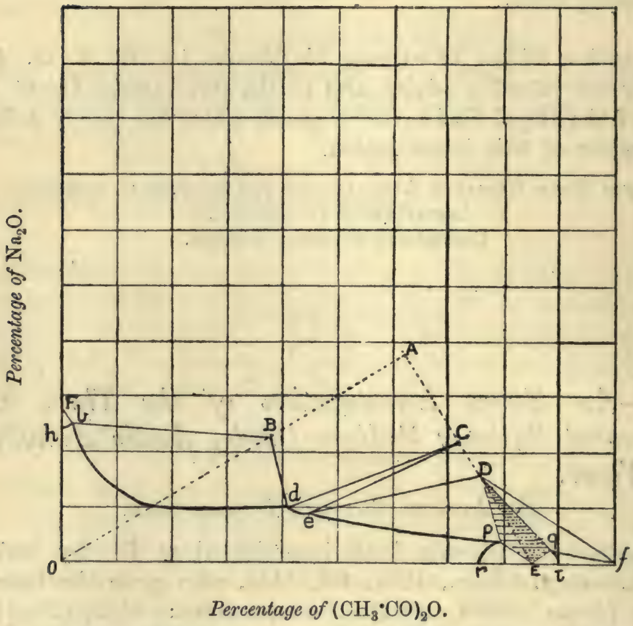
(2) The system appeared of especial interest, because, according to the same author, the saturation curve of the acid salt, $C_2H_3O_2Na,C_2H_4O_2$, is divided into two parts, separated by the saturation curve of the acid salt, $C_2H_3O_2Na,2C_2H_4O_2$. This means

that there are two distinct saturated solutions, in contact with which the compounds $C_2H_3O_2Na,C_2H_4O_2$ and $C_2H_3O_2Na,2C_2H_4O_2$ can exist in equilibrium at constant temperature, and it would appear that the addition of either water or acetic anhydride to a solution of sodium acetate in pure acetic acid tends merely to dilute the acid and bring about the formation of the salt containing only one molecule of acetic acid.

The system has been completely investigated at 0°, 15°, 30°, 45°,

FIG. 1.

0°.



$F = NaOH,4H_2O$. $A = C_2H_3O_2Na$. $B = C_2H_3O_2Na,3H_2O$. $C = C_2H_3O_2Na,C_2H_4O_2$. $D = C_2H_3O_2Na,2C_2H_4O_2$. $E = C_2H_4O_2$.

60°, and 75°, and partly at 5° and 20°. The temperature never varied more than 0·1° during any experiment.

The nature of the solid phase has been determined by Schreinemakers' residue method (*Zeitsch. physikal. Chem.*, 1892, **9**, 57), in which both the solution and the wet solid (the residue) in contact with it are analysed. The two points obtained by plotting the compositions of the solution and residue respectively should lie in a straight line with the point representing the composition of the pure solid phase.

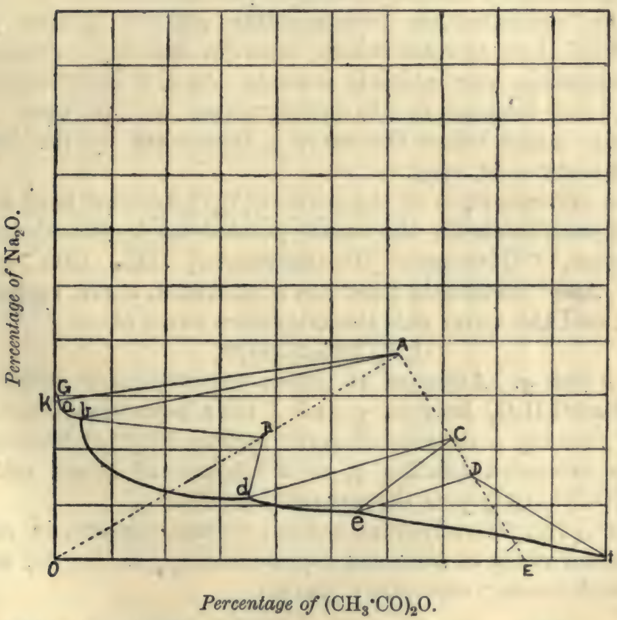
Other experimental evidence has been used when necessary.

The appearance of the solid phase is generally a clear indication of its nature, since all the compounds have a definite crystalline form, as follows:

$C_2H_3O_2Na$ = scaly plates.
$C_2H_3O_2Na,3H_2O$ = rhombic prisms.
$C_2H_3O_2Na,C_2H_4O_2$ = rectangular prisms.
$C_2H_3O_2Na,2C_2H_4O_2$ = fine needles.

FIG. 2.

15°.



$G = NaOH,3\frac{1}{2}H_2O$. $A = C_2H_3O_2Na$. $B = C_2H_3O_2Na,3H_2O$. $C = C_2H_3O_2Na,C_2H_4O_2$. $D = C_2H_3O_2Na,2C_2O_4O_2$. $E = C_2H_4O_2$.

The samples were analysed in such a way that the free acid or alkali was titrated, whilst the sodium was estimated as chloride, a duplicate analysis being made in each case.

All data concerning the compounds of sodium oxide and water are taken from Pickering's figures (Trans., 1893, **63**, 890).

The isotherms obtained are shown diagrammatically in Figs. 1 to 6. In these figures all possible mixtures of sodium acetate and water lie on the line *OA*. All mixtures of solid and solution, or solutions, on the left of *OA* are alkaline, and all those on the right of it are acid. All mixtures of sodium acetate and acetic acid lie on the line *AE*, whilst to the right of this lie all mixtures containing free acetic anhydride. Between *OA* and *AE* lie all mixtures of sodium acetate, acetic acid, and water.

At 0° (Fig. 1) the solubility of the compound $NaOH,4H_2O$ is only slightly affected by the presence of the compound

$$C_2H_3O_2Na,3H_2O$$

to saturation; *b* represents a solution saturated with respect to $C_2H_3O_2Na,3H_2O$ and $NaOH,4H_2O$; $C_2H_3O_2Na,3H_2O$ is the stable phase over the long range of concentrations represented by the line *bd*, extending well into the acid portion of the diagram. *bd* is the saturation curve of $C_2H_3O_2Na,3H_2O$ in all the figures.

At the concentration corresponding with *d*, a new phase, $C_2H_3O_2Na,C_2H_4O_2$, appears, which, however, has only a small range of concentrations over which it is stable. At *e*, $C_2H_3O_2Na,2C_2H_4O_2$ appears, and remains as the stable phase up to pure acetic anhydride, except where the curve is intersected by the freezing curve of acetic acid, *rpqt*.

At the extreme right of the curve, $C_2H_3O_2Na$ must have a small range of saturations for the reason pointed out by Schreinemakers (Roozeboom, "Heterogene Gleichgewichte," III., 1911 edition, p. 208). At 0° acetic acid itself has a saturation curve, represented by *rpqt*, and this curve cuts the saturation curve of

$$C_2H_3O_2Na,2C_2H_4O_2$$

(*ef*) in *p* and *q*. Attempts to obtain supersaturated solutions of $C_2H_3O_2Na,2C_2H_4O_2$ between *p* and *q* have been unsuccessful, the solution forming a mixture of acetic acid and $C_2H_3O_2Na,2C_2H_4O_2$, plus the saturated solution *p*, or a mixture of acetic acid and $C_2H_3O_2Na,2C_2H_4O_2$, plus the saturated solution *q*.

At 15° (Fig. 2) anhydrous sodium acetate appears, in contact with a small range of solutions, represented by the line *ab*, and we have the following saturation curves:

bd corresponding with $C_2H_3O_2Na,3H_2O$
de „ „ $C_2H_3O_2Na,C_2H_4O_2$
ef „ „ $C_2H_3O_2Na,2C_2H_4O_2$.

The isotherm at 30° (Fig. 3) is of particular interest because the author has been unable to confirm the results of Dukelski (*loc. cit.*). According to that author, $C_2H_3O_2Na,3H_2O$ is dehydrated by sodium hydroxide, giving $C_2H_3O_2Na,\frac{1}{2}H_2O$. Further, Dukelski states that $C_2H_3O_2Na,C_2H_4O_2$ has a second saturation curve. Special attention has been devoted to these points:

(1) *The dehydration of* $C_2H_3O_2Na,3H_2O$.

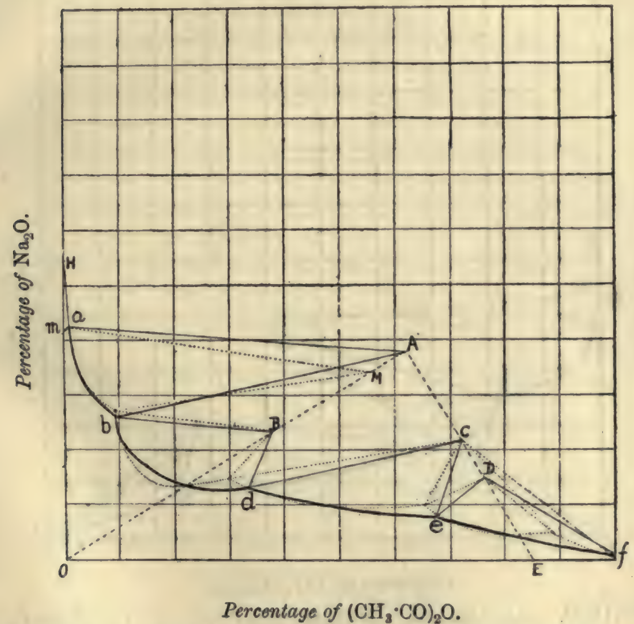
The residue method shows that $C_2H_3O_2Na$ is undoubtedly the solid phase produced by the dehydration. $C_2H_3O_2Na,3H_2O$ melts at the same temperature alone or mixed with anhydrous sodium acetate.

(2) *The recurrence of* $C_2H_3O_2Na,C_2H_4O_2$ *in stronger acid solutions.*

Both the residue method and the appearance of the solid phase point to the uninterrupted existence of $C_2H_3O_2Na,2C_2H_4O_2$ in high concentrations of acetic anhydride. As already mentioned, $C_2H_3O_2Na,C_2H_4O_2$ separates out in prisms, and $C_2H_3O_2Na,2C_2H_4O_2$ in needles. At higher temperatures, where a recurrence of the $C_2H_3O_2Na,C_2H_4O_2$ curve was obtained, the prisms were unmistakable. The solid phase in solutions of acetic anhydride at 30° was dried, and its composition and melting point were practically identical with those of $C_2H_3O_2Na,2C_2H_4O_2$. Dukelski did not determine the composition of solutions saturated with respect to two solid phases, and the isotherm plotted from his figures and shown in dotted lines in Fig. 3 differs materially from that obtained by the author.

FIG. 3.

30°.



H=$NaOH,1H_2O$. *A*=$C_2H_3O_2Na$. *B*=$C_2H_3O_2Na,3H_2O$. *C*=$C_2H_3O_2Na,C_2H_4O_2$. *D*=$C_2H_3O_2Na,2C_2H_4O_2$. *M*=$C_2H_3O_2Na,\frac{1}{2}H_2O$. *E*=$C_2H_4O_2$.

At 45° (Fig. 4) the field of $C_2H_3O_2Na,3H_2O$ is rapidly narrowing, for the transition temperature of $C_2H_3O_2Na,3H_2O$ and $C_2H_3O_2Na$ in the two component system is 58°. $C_2H_3O_2Na,C_2H_4O_2$ has now two saturation curves, *de* and *fg*, separated by *ef*, the saturation curve of $C_2H_3O_2Na,2C_2H_4O_2$.

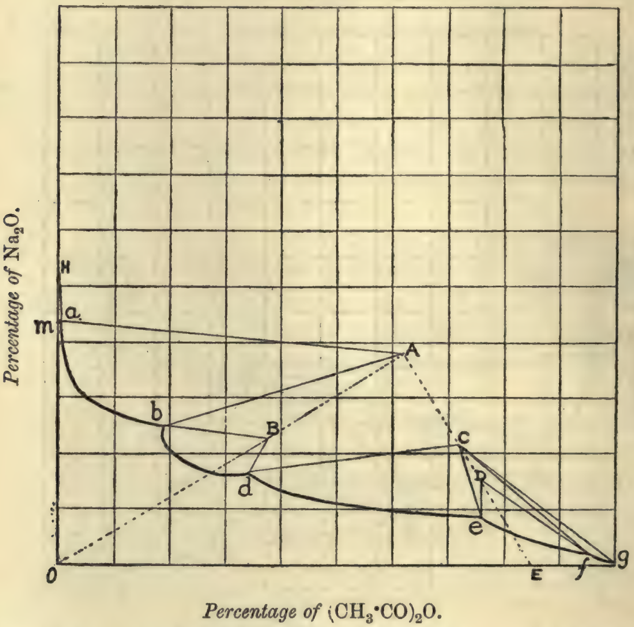
This exists only in the region of solutions containing a maximum quantity of acetic acid, and there are two saturated solutions, *e* and *f*, in contact with which $C_2H_3O_2Na,C_2H_4O_2$ and

$$C_2H_3O_2Na,2C_2H_4O_2$$

can exist simultaneously. The composition of the former solution can be expressed in terms of sodium acetate, acetic acid, and water, and that of the latter in terms of sodium acetate, acetic acid, and acetic anhydride.

FIG. 4.

45°.

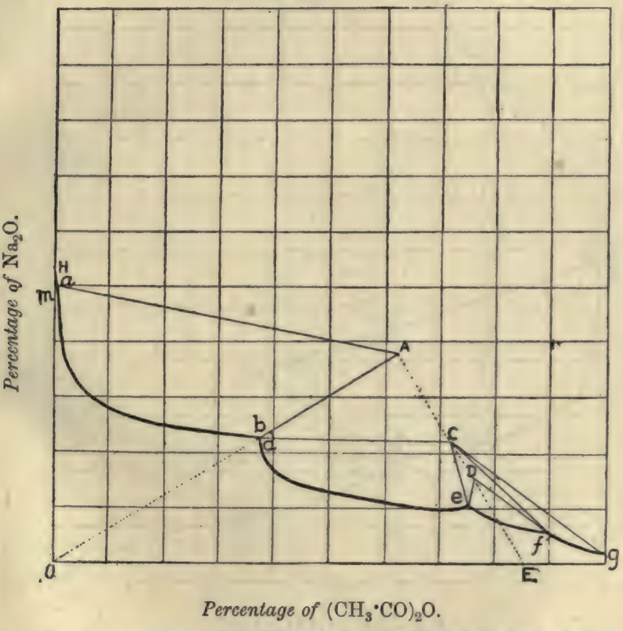


H=$NaOH,1H_2O$. *A*=$C_2H_3O_2Na$. *B*=$C_2H_3O_2Na,3H_2O$. *C*=$C_2H_3O_2Na,C_2H_4O_2$. *D*=$C_2H_3O_2Na,2C_2H_4O_2$. *E*=$C_2H_4O_2$.

At 60° (Fig. 5) $C_2H_3O_2Na,3H_2O$ can no longer exist, since it melts alone at 58°. $C_2H_3O_2Na,C_2H_4O_2$ and $C_2H_3O_2Na$ can now, therefore, exist together in contact with the solution represented by *b* (or *d*). This point lies on the neutral line *AO*, and the addition of acid to a saturated solution of $C_2H_3O_2Na$ in water causes immediate separation of $C_2H_3O_2Na,C_2H_4O_2$. The latter compound still has two saturation curves, *de* and *fg*, separated by the curve *ef* corresponding with saturated solutions of $C_2H_3O_2Na,2C_2H_4O_2$, and there are two saturated solutions in contact with which $C_2H_3O_2Na,C_2H_4O_2$ and $C_2H_3O_2Na,2C_2H_4O_2$ can exist together. One of these, *e*, may be represented in terms of sodium acetate, acetic acid, and water; the other, *f*, in terms of sodium acetate, acetic acid, and acetic anhydride.

FIG. 5.

60°.



H = $NaOH,1H_2O$. *A* = $C_2H_3O_2Na$. *C* = $C_2H_3O_2Na,C_2H_4O_2$
D = $C_2H_3O_2Na,2C_2H_4O_2$. *E* = $C_2H_4O_2$.

At 75° (Fig. 6) we have only two phases containing acetic anhydride, namely, $C_2H_3O_2Na$, represented by *ab*(*ad*), and $C_2H_3O_2Na,C_2H_4O_2$, represented by *dg*(*bg*).

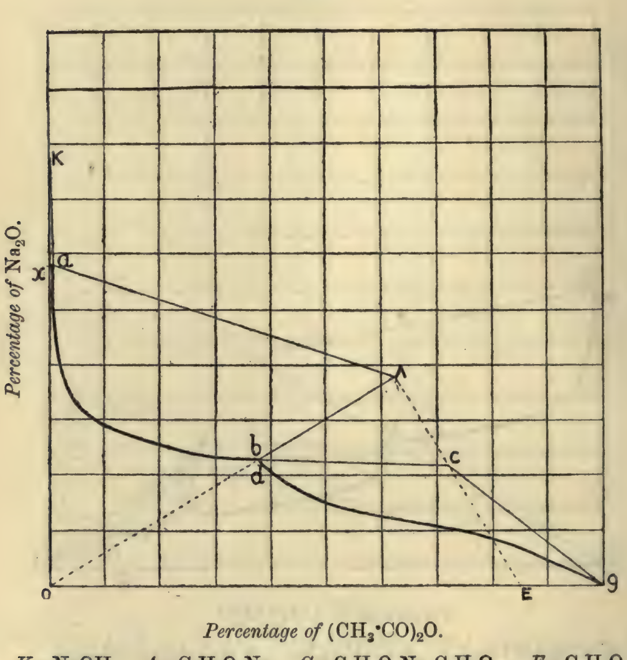
The space model in which all these isotherms are plotted against the temperature is shown diagrammatically in Fig. 7.

Adjoining the fields of NaOH, $NaOH,1H_2O$, $NaOH,2H_2O$, and $NaOH,3\frac{1}{2}H_2O$ is the field in which the anhydrous salt, $C_2H_3O_2Na$, is stable. This field is bounded on the right by the field of

$C_2H_3O_2Na,3H_2O$, which ends at the point *P* (58°), the melting point of $C_2H_3O_2Na,3H_2O$ in the two component system, sodium acetate–water. Above the point *P* the field of $C_2H_3O_2Na$ is bounded by the neutral line, beyond which $C_2H_3O_2Na,C_2H_4O_2$ exists. In no case could a field of saturation of $C_2H_3O_2Na,\frac{1}{2}H_2O$ be observed, which, if it exists, must be formed from the trihydrate before the anhydrous salt, and must have a field lying between the fields of these other compounds, namely, $C_2H_3O_2Na$ and $C_2H_3O_2Na,3H_2O$.

FIG. 6.

75°.



K = NaOH. *A* = $C_2H_3O_2Na$. *C* = $C_2H_3O_2Na,C_2H_4O_2$. *E* = $C_2H_4O_2$.

Also, if there is a hemihydrate, the addition of a saturated solution of $C_2H_3O_2Na,3H_2O$ at 50° to a quantity of anhydrous salt should cause a rise of temperature to the transition temperature of $C_2H_3O_2Na,\frac{1}{2}H_2O$ and $C_2H_3O_2Na$, and the addition of a large quantity of anhydrous salt to the half-melted mass at *P* should cause a temperature change. This is, however, not the case.

The lowest temperature at which $C_2H_3O_2Na,3H_2O$ is dehydrated by sodium hydroxide is 11·2°. At this transition point *R*, a saturated solution of sodium hydroxide can exist with solid

$C_2H_3O_2Na,3H_2O$

and the anhydrous salt.

The compound $C_2H_3O_2Na,2C_2H_4O_2$ melts at 74·8°, giving

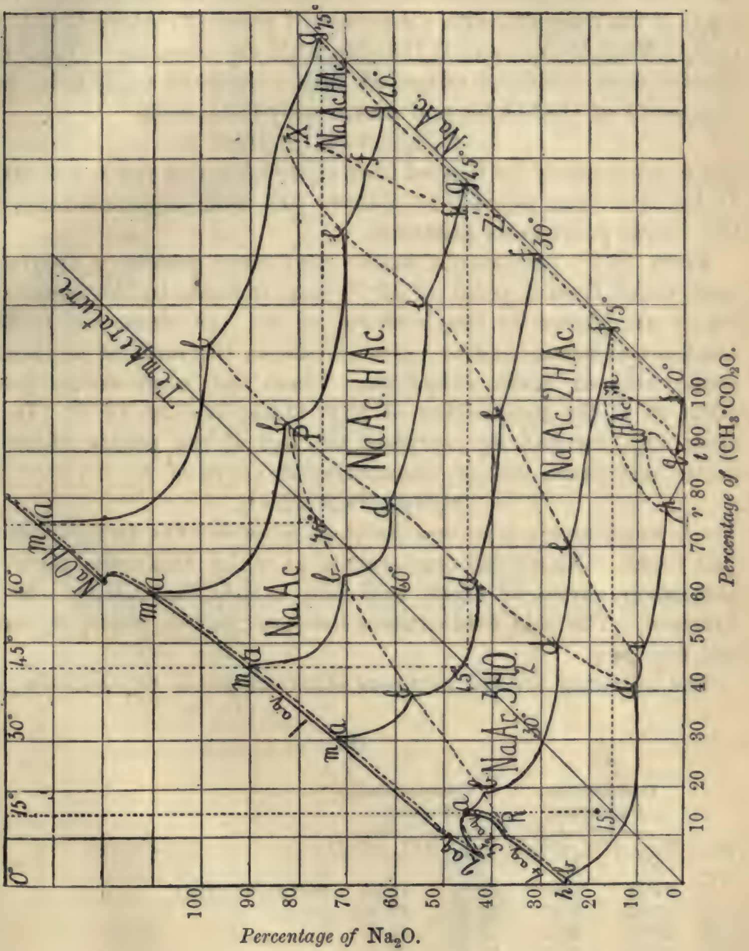


FIG. 7.

$C_2H_3O_2Na,C_2H_4O_2$ and acetic acid. Since its maximum stability is in the two component system $C_2H_3O_2Na—C_2H_4O_2$, the limit of its field is at the point *X*, where the saturation curve at 74·8° is cut by the line *AE*, on which lie all mixtures of acetic acid and sodium acetate. Above this temperature the field of $C_2H_3O_2Na,C_2H_4O_2$

extends throughout the acid portion of the diagram. Below this temperature the field of $C_2H_3O_2Na,2C_2H_4O_2$ is bounded for a time on each side by the field of $C_2H_3O_2Na,C_2H_4O_2$. The exact point at which $C_2H_3O_2Na,C_2H_4O_2$ ceases to exist in contact with acetic anhydride solutions is difficult to obtain experimentally. Strictly speaking, there should be a field of $C_2H_3O_2Na$ on the extreme right hand of the diagram, with a non-variant point (*Z*) where $C_2H_3O_2Na$, $C_2H_3O_2Na,C_2H_4O_2$, and $C_2H_3O_2Na,2C_2H_4O_2$ co-exist. This field should show solutions saturated with respect to $C_2H_3O_2Na$, or a compound of $C_2H_3O_2Na$ and acetic anhydride, since

$$C_2H_3O_2Na,2C_2H_4O_2$$

could not possibly be formed from $C_2H_3O_2Na$ and acetic anhydride. It has not been possible to observe this field experimentally, but the curves point to its existence.

From 16·7° downwards, acetic acid must possess a saturation field which from a point at 16·7° must increase to the boundaries which are shown in the isotherm at 0°. *rn* shows the locus of solutions of acetic acid in water; *tn* shows the locus of solutions of acetic acid in acetic anhydride. These loci must merge into a point at *n*, the composition of pure acetic acid at 16·7°. In the same way, *wp* and *wq* represent the loci of the points where the acetic acid curve cuts *ef*, the saturation curve of

$$C_2H_3O_2Na,2C_2H_4O_2.$$

These must merge into one point at *w*, where the two curves will just touch. Above the temperature at which this takes place, the saturation curves of acetic acid and $C_2H_3O_2Na,2C_2H_4O_2$ will not intersect. The acid field extends between the two boundary curves *rnt* and *pwq*.

The following are the numbers obtained in the experiments:

0°.

	Composition of solution.		Composition of residue.		
No.	Na_2O. %	$(CH_3\cdot CO)_2O$. %	Na_2O. %	$(CH_3\cdot CO)_2O$. %	Solid phase.
1	24·12	2·04	23·52	18·04	$C_2H_3O_2Na,3H_2O$
2	22·55	2·52	22·69	18·24	,,
3	19·82	3·83	22·23	30·35	,,
4	14·46	8·55	19·76	26·95	,,
5	10·07	16·56	—	—	,,
6	9·81	24·56	19·52	34·26	,,
7	9·72	31·00	21·06	36·95	,,
8	9·77	33·28	21·45	36·70	,,
9	9·76	37·6	20·89	37·61	,,
10	9·75	40·00	21·29	38·14	,,
11	9·77	41·23	20·51	41·35	$C_2H_3O_2Na,3H_2O+C_2H_3O_2Na,C_2H_4O_2$
12	9·04	43·94	17·56	62·71	$C_2H_3O_2Na,C_2H_4O_2$
13	8·96	44 80	16·10	63·57	$C_2H_3O_2Na,C_2H_4O_2+C_2H_3O_2Na,2C_2H_4O_2$

0° (*continued*).

	Composition of solution.		Composition of residue.		
No.	Na_2O. %	$(CH_3{\cdot}CO)_2O$. %	Na_2O. %	$(CH_3{\cdot}CO)_2O$. %	Solid phase.
14	8·72	45·10	12·64	64·97	$C_2H_3O_2Na,2C_2H_4O_2$
15	7·83	50·03	13·02	66·15	,,
16	7·00	55·92	12·19	68·25	,,
17	6·31	59·80	—	—	,,
18	6·26	60·64	—	—	,,
19	6·19	62·44	9·70	67·75	,,
20	5·66	64·79	10·65	71·02	,,
21	4·95	71·13	10·02	74·07	,,
22	4·02	79·29	6·93	78·25	,,
23	1·05	92·29	3·53	88·70	,,
24	0·95	93·67	6·14	87·72	,,
25	0·74	94·66	4·04	90·33	,,
26	0·57	96·16	3·21	91·22	,,
27	0·42	97·51	1·51	95·58	,,
28	—	75·31	—	—	$C_2H_4O_2$
29	2·01	76·42	1·23	81·28	,,
30	2·01	76·06	0·95	81·58	,,
31	2·49	76·34	—	—	,,
32	2·33	77·30	1·87	81·66	,,
33	3·48	77·67	—	—	,,
34	—	90·34	—	—	,,
35	1·14	90·31	0·45	87·93	,,
36	1·41	90·07	0·47	87·56	,,
37	1·84	88·97	—	—	,,
38	2·06	87·64	1·60	87·14	,,
39	2·19	87·90	2·25	86·33	$C_2H_4O_2 + C_2H_3O_2Na,2C_2H_4O_2$

5°.

No.	Na_2O. %	$(CH_3{\cdot}CO)_2O$. %	Na_2O. %	$(CH_3{\cdot}CO)_2O$. %	Solid phase.
40	10·14	28·41	20·82	35·89	$C_2H_3O_2Na,3H_2O$
41	10·08	40·24	18·82	54·93	$C_2H_3O_2Na,3H_2O + C_2H_3O_2Na,C_2H_4O_2$
42	9·03	43·89	18·26	64·00	$C_2H_3O_2Na,C_2H_4O_2$
43	8·88	46·38	18·86	66·11	,,
44	8·23	49·73	12·63	64·28	$C_2H_3O_2Na,2C_2H_4O_2$
45	6·72	58·83	12·49	68·63	,,
46	4·56	75·98	12·34	75·79	,,
47	3·56	80·47	8·79	78·89	,,
48	1·25	92·88	11·56	80·61	,,

20°.

No.	Na_2O. %	$(CH_3{\cdot}CO)_2O$. %	Na_2O. %	$(CH_3{\cdot}CO)_2O$. %	Solid phase.
49	5·01	76·58	11·60	75·11	$C_2H_3O_2Na,2C_2H_4O_2$
50	4·89	77·33	9·97	76·72	,,
51	4·36	80·12	11·74	77·17	,,
52	3·19	84·31	10·97	78·92	,,
53	2·10	89·75	9·67	81·25	,,
54	1·88	89·88	11·68	79·68	,,
55	1·33	92·77	12·19	79·15	,,

15°.

No.	Na_2O. %	$(CH_3{\cdot}CO)_2O$. %	Na_2O. %	$(CH_3{\cdot}CO)_2O$. %	Solid phase.
56	29·34	0·15	30·86	13·69	$C_2H_3O_2Na$
57	25·94	4·19	24·12	24·35	$C_2H_3O_2Na,3H_2O$
58	22·24	4·88	22·96	27·47	,,
59	15·49	12·01	19·18	24·81	,,
60	11·45	23·54	—	—	,,

15° (*continued*).

No.	Composition of solution.		Composition of residue.		Solid phase.
	Na_2O. %	$(CH_3\cdot CO)_2O$. %	Na_2O. %	$(CH_3\cdot CO)_2O$. %	
61	11·25	34·56	18·60	55·59	$C_2H_3O_2Na,3H_2O + C_2H_3O_2Na,C_2H_4O_2$
62	10·33	39·08	18·98	64·16	$C_2H_3O_2Na,C_2H_4O_2$
63	10·24	39·73	18·27	62·16	,,
64	9·16	49·32	16·85	63·51	,,
65	8·56	54·34	14·72	66·82	$C_2H_3O_2Na,C_2H_4O_2 + C_2H_3O_2Na,2C_2H_4O$
66	7·06	61·63	—	—	$C_2H_3O_2Na,2C_2H_4O_2$
67	6·17	68·81	9·11	71·42	,,
68	5·95	70·55	13·13	74·48	,,
69	5·52	73·02	10·64	74·79	,,
70	4·84	77·60	11·22	77·26	,,
71	3·44	84·15	9·68	79·91	,,
72	2·87	86·61	10·75	79·80	,,
73	2·16	90·56	10·16	82·28	,,
74	1·02	95·87	10·75	81·90	,,
75	0·79	98·09	—	—	,,

30°.

No.	Na_2O. %	$(CH_3\cdot CO)_2O$. %	Na_2O. %	$(CH_3\cdot CO)_2O$. %	Solid phase.
76	35·31	0·77	36·00	11·98	$C_2H_3O_2Na$
77	26·25	8·92	28·65	18·28	,,
78	25·98	9·06	23·68	27·54	$C_2H_3O_2Na,3H_2O$
79	18·09	13·62	21·79	31·80	,,
80	13·53	21·88	19·99	32·72	,,
81	13·24	33·05	19·56	52·78	$C_2H_3O_2Na,3H_2O + C_2H_3O_2Na,C_2H_4O_2$
82	13·14	32·90	18·48	55·93	$C_2H_3O_2Na,C_2H_4O_2$
83	7·64	65·07	—	—	,,
84	7·67	66·42	11·74	69·37	$C_2H_3O_2Na,C_2H_4O_2 + C_2H_3O_2Na\ 2C_2H_4O_2$
85	7·33	69·68	—	—	$C_2H_3O_2Na,2C_2H_4O_2$
86	6·94	71·39	9·50	72·78	,,
87	6·61	72·85	—	—	,,
88	5·52	77·76	11·31	77·02	,,
89	3·78	83·92	11·91	78·42	,,
90	2·94	86·73	11·60	79·34	,,
91	2·70	88·61	10·94	80·31	,,
92	1·27	94·78	10·72	81·80	,,

45°.

No.	Na_2O. %	$(CH_3\cdot CO)_2O$. %	Na_2O. %	$(CH_3\cdot CO)_2O$. %	Solid phase.
93	39·82	0·77	39·51	24·84	$C_2H_3O_2Na$
94	32·69	2·04	35·28	27·31	,,
95	28·86	6·53	30·60	14·89	,,
96	25·58	14·29	27·62	21·62	,,
97	23·12	18·70	22·72	31·80	$C_2H_3O_2Na,3H_2O$
98	22·46	18·85	22·53	26·75	,,
99	21·12	19·44	22·11	30·99	,,
100	16·04	26·39	—	—	,,
101	16·00	33·87	21·18	46·58	$C_2H_3O_2Na,3H_2O + C_2H_3O_2Na,C_2H_4O_2$
102	14·12	36·28	18·21	55·45	$C_2H_3O_2Na,C_2H_4O_2$
103	12·61	41·12	19·35	63·66	,,
104	11·81	44·85	16·33	57·24	,,
105	10·84	51·00	16·70	62·27	,,
106	10·15	55·68	17·48	66·49	,,
107	10·32	56·37	16·39	64·03	,,
108	9·34	61·49	17·52	68·27	,,
109	9·04	65·11	16·81	69·27	,,
110	8·86	65·74	16·33	69·54	,,

45° (*continued*).

No.	Composition of solution.		Composition of residue.		Solid phase.
	Na_2O. %	$(CH_3 \cdot CO)_2O$. %	Na_2O. %	$(CH_3 \cdot CO)_2O$. %	
111	8·63	68·21	15·89	70·21	C_2H_3O Na,$C_2H_4O_2$
112	8·54	70·06	18·20	71·79	,,
113	8·20	75·06	16·06	73·27	,,
114	5·54	82·16	9·52	79·34	$C_2H_3O_2Na$ $2C_2H_4O_2$
115	4·64	83·64	8·59	80·87	,,
116	4·25	85·38	6·37	83·54	,,
117	4·20	86·39	9·82	80·18	,,
118	2·36	94·23	10·37	83·40	,,
119	1·19	97·19	9·92	85·81	$C_2H_3O_2Na,C_2H_4O_2$
120	0·93	98·37	11·95	84·89	,,

60°.

121	46·22	0·0	44·92	16·01	$C_2H_3O_2Na$
122	36·25	1·83	37·63	21·93	,,
123	35·55	2·07	36·18	9·24	,,
124	34·60	2·83	35·16	10·44	,,
125	31·38	4·56	33·32	20·89	,,
126	29·31	7·96	32·99	33·51	,,
127	26·60	14·31	34·25	45·52	,,
128	26·26	15·58	29·80	29·43	,,
129	23·90	25·73	26·85	33·54	,,
130	21·99	36·17	—	—	,,
131	17·75	37·41	20·20	57·64	$C_2H_3O_2Na,C_2H_4O_2$
132	12·57	49·62	19·04	65·14	,,
133	10·73	60·84	19·18	69·26	,,
134	10·27	64·23	19·19	70·36	,,
135	9·86	66·97	18·55	70·92	,,
136	10·47	74·62	18·42	71·93	,,
137	8·31	77·83	13·70	76·80	$C_2H_3O_2Na,2C_2H_4O_2$
138	6·07	84·44	—	—	,,
139	5·74	85·71	10·30	81·54	,,
140	4·25	90·22	16·52	77·49	$C_2H_3O_2Na,C_2H_4O_2$
141	3·08	94·46	20·87	73·27	,,

75°.

142	44·45	0·76	43·78	15·54	$C_2H_3O_2Na$
143	39·40	2·12	39·09	27·64	,,
144	35·37	3·24	36·45	29·12	,,
145	32·47	5·03	34·67	25·10	,,
146	27·38	15·45	29·30	23·90	,,
147	24·48	26·47	28·87	36·96	,,
148	22·30	36·69	—	—	,,
149	17·85	43·06	19·91	57·61	$C_2H_3O_2Na,C_2H_4O_2$
150	12·78	56·53	18·15	65·66	,,
151	12·13	58·69	—	—	,,
152	11·05	65·71	15·67	68·58	,,
153	10·54	68·56	17·63	70·88	,,
154	8·84	77·37	15·48	74·65	,,
155	9·02	78·28	—	—	,,
156	8·61	78·75	16·89	74·52	,,
157	7·63	81·49	15·17	76·32	,,
158	4·09	89·61	13·75	79·99	,,
159	3·63	90·72	11·66	82·32	,,
160	0·44	98·35	—	—	,,

In conclusion, the author wishes to thank Professor Sir William Ramsay for various suggestions, and for his kindness in revising this paper for publication.

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LIV.—*Researches on Bleaching Powder. Part II. The Action of Dilute Acids on Bleaching Powder.*

By Robert Llewellyn Taylor and Clifford Bostock.

Much discussion has taken place from time to time as to the action of dilute acids on bleaching powder. Long ago, Gay Lussac stated that a colourless solution of pure hypochlorous acid could be obtained by acidulating a solution of bleaching powder with dilute nitric acid, and then distilling it (*Ann. Chim. Phys.*, 1849, [iii], **26**, 163). On the other hand, Goepner (*Dingl. Polyt. J.*, 1873, **209**, 204) asserted that on decomposition with acids bleaching powder simply decomposes into its constituents (chlorine and lime), yielding chlorine and no hypochlorous acid. In 1874 Schorlemmer took part in the discussion (*Journ. Chem. Soc.*, **27**, 335), confirming Gay Lussac's observation, and pointing out that the students in Owens College prepared hypochlorous acid by Gay Lussac's method as part of their regular course.

This uncertainty was doubtless mainly due to the fact that no satisfactory method of distinguishing between free chlorine and hypochlorous acid was known at the time, most trust apparently being placed in the reaction with mercury, with which hypochlorous acid was said to produce an oxychloride, whereas chlorine did not.

Kopfer (*Journ. Chem. Soc.*, 1875, **28**, 713), trying to decide between these contradictory statements, investigated the action of dilute nitric, sulphuric, and hydrochloric acids on bleaching powder. He prepared the bleaching powder himself, but according to his analysis it was a very different substance from the ordinary commercial article, as it contained more than 50 per cent. of free lime.

Kopfer summarised his results as follows:

"If to a solution of bleaching powder, or to the same substance in the dry state, a dilute mineral acid, such as nitric, hydrochloric, or sulphuric be added in such quantity as to saturate the caustic lime and to decompose the hypochlorite supposed to be present according to Gay-Lussac's hypothesis, then, on distillation, an aqueous solution of almost chemically pure chlorine monoxide is obtained, which amounts in the most favourable case to about 92 per cent. of the chlorine monoxide as corresponding with the theoretical hypochlorite."

Recently one of us (Taylor, Trans., 1910, **97**, 2541) described a method of distinguishing between hypochlorous acid and free chlorine, and of determining the proportions of each in a mixture of the two. The method depends on the fact that, for the same amount of chlorine present, the oxidising action of hypochlorous acid is twice as great as that of free chlorine. To a mixture of the two substances an excess of sodium arsenite is added. The liquid is then divided into two equal parts; in one part the amount of arsenite oxidised is determined, and in the other the amount of chloride produced. The proportions of the two substances in the mixture can then easily be calculated.

In the present investigation the above very simple and yet fairly accurate method has been applied to a repetition of some of Kopfer's experiments, extending it also to the action of acids other than those described by him. In all these experiments the chloride present in the second half of the arsenite solution was determined by Volhard's method, which is certainly more rapid and apparently quite as trustworthy as the one described in the former paper.

The bleaching powder used for most of the experiments was a fair average sample, analysis of which gave the following figures:

Total chlorine = 39·05 per cent.
Available chlorine = 34·63 ,,
Total lime (CaO) = 44·9 ,,
Free lime = 13·1 ,,

Assuming the bleaching powder to consist of calcium chloride and calcium hypochlorite, then 100 grams of it would contain 34·4 grams of the latter. Also 10 grams of it (the amount taken in practically all the experiments) would require 46·8 c.c. of *N*-acid to neutralise the whole of the free lime, and 48·8 c.c. more to decompose the whole of the calcium hypochlorite present, a total of 95·6 c.c.

In each experiment 10 grams of bleaching powder were rubbed with water, and then the desired volume of acid was added slowly from a burette, the mixture being continually shaken, in order to avoid, so far as possible, local excess of acid. (It is difficult to do this entirely, however, and this doubtless accounts, to some extent, for some of the irregularities in the results.) The whole was then distilled from a flask of about 1 litre capacity, the vapours being passed through a small condenser. A few drops of the distillate were allowed to escape, and then 20 c.c. were collected. For determining the amounts of hypochlorous acid and chlorine, 10 c.c. only of this were used.

As one would anticipate, the amount of water, and thus the extent of dilution of the acid, makes a considerable difference in the results, and, in order to ascertain what was the best amount of water to use, some experiments were made, using 10 grams of bleaching powder and 50 c.c. of *N*-sulphuric acid for each experiment, but varying the amount of water. It was found that with quantities of water varying from 50 c.c. to 200 c.c. considerably more free chlorine was produced than with larger amounts, and in all the subsequent experiments 300 c.c. of water were always used.

In the following tables, where two or more sets of figures are given they relate to separate experiments.

TABLE I.

Distillation with Sulphuric Acid.

Volume of N-H_2SO_4, in c.c.	Arsenite oxidised.	Chloride produced.	Hypo-chlorous acid, per cent.	Chlorine, per cent.
30	0·4	0·2	100·0	0·0
40	6·8	3·45	97·0	3·0
50	8·65	4·5	92·2	7·8
	9·15	4·75	92·6	7·4
60	16·3	8·85	84·2	15·8
	16·05	8·8	82·4	17·6
70	24·55	14·4	70·5	29·5
	24·6	14·15	73·8	26·2
80	30·65	17·55	74·6	25·4
	31·05	17·9	73·5	26·5
90	34·1	19·35	76·0	24·0
	33·4	18·8	77·7	22·3
100	24·0	14·0	71·4	28·6
	28·55	17·1	67·0	33·0
150	10·15	8·3	22·3	77·7
	10·75	8·75	22·9	77·1
200	7·05	7·25	0·0	100·0
	9·1	9·35	0·0	100·0

It may be pointed out that in the above table the figures in the column headed "arsenite oxidised" afford an indication of the amount of hypochlorous acid (or hypochlorous acid and chlorine) in the distillate. As 10 c.c. of the distillate were used in each determination, and as the solution of arsenite was *N*/10, and, further, as the "arsenite oxidised" represents the amount in half of the solution, it is plain that, using 50 c.c. of *N*-sulphuric acid, a distillate is obtained which is $N/10 \times 1{\cdot}7$ or 1·8. A decinormal solution of hypochlorous acid would contain 2·62 grams of HOCl per litre, or 0·262 per cent., so that the distillate referred to would contain about 4·5 grams of HOCl per litre. It will be observed that with 80 or 90 c.c. of acid the distillate is much stronger, but it contains a greater proportion of chlorine.

The figures representing the proportion of hypochlorous acid and chlorine in the distillate are not of much value beyond the point where 70 c.c. of acid were used, because, as the amount of free chlorine increases, the whole of it is not condensed in the distillate. It begins to escape about the point referred to, and, as the amount of acid is further increased, more and more, and finally most of it, escapes.* Therefore, in the accompanying curve, the progress of the alteration in the reaction is indicated by the gradual diminution of the amount of hypochlorous acid. These remarks apply to the cases of the other mineral acids as well.

TABLE II.

Distillation with Hydrochloric Acid.

Volume of *N*-HCl, in c.c.	Arsenite oxidised.	Chloride produced.	Hypo-chlorous acid, per cent.	Chlorine, per cent.
40	4·0	2·0	100·0	0·0
50	11·25	5·8	94·0	6·0
	11·2	5·75	94·8	5·2
60	17·4	9·5	83·2	16·8
	17·0	9·45	80·0	20·0
70	24·2	14·1	71·6	28·4
	24·4	14·05	73·7	26·3
80	29·25	17·0	72·1	27·9
	29·3	17·0	72·4	27·6
90	27·6	16·5	67·3	32·7
	29·1	17·25	68·7	31·3
100	21·65	13·05	65·9	34·1
	21·3	13·0	63·8	36·2
120	9·5	8·15	16·6	83·4
	8·75	7·8	12·2	87·8
130	6·9	6·9	0·0	100·0

---

* The irregular way in which the free chlorine escapes is probably one of the causes of the observed irregularities in the results.

TABLE III.

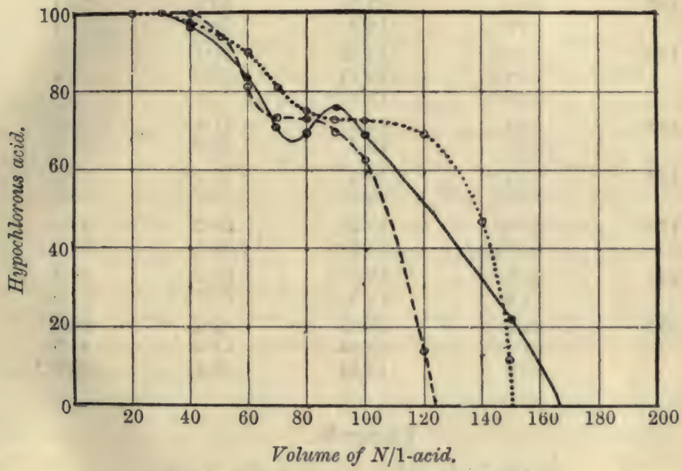
Distillation with Nitric Acid.

Volume of *N*-acid, in c.c.	Arsenite oxidised.	Chloride produced.	Hypo-chlorous acid, per cent.	Chlorine, per cent.
20	0·1	0·05	100·0	0·0
30	0·1	0·05	100·0	0·0
40	4·45	2·25	98·0	2·0
50	11·8	6·1	93·4	6·6
	11·1	5·65	96·5	3·5
60	17·55	9·25	89·7	10·3
	13·5	7·05	91·5	8·5
70	20·6	11·35	81·5	18·5
	22·05	12·15	81·5	18·5
80	28·2	16·1	75·2	24·8
	28·85	16·25	77·5	22·5
90	34·5	20·75	70·6	29·4
	36·4	20 65	76·2	23·8
	29·2	16·8	73·8	26·4
100	36·85	21·4	72·2	27·8
	38·0	21·75	74·7	25·3
120	21·6	12·85	68·1	31·9
	24·4	14·1	73·0	27·0
140	13·0	8·7	49·5	50·5
	12·75	8·9	43·3	56·7
150	7·6	7·4	2·7	97·3
	8·2	7·3	12·3	87·7
	7·85	7·0	12·1	87·9
160	7·1	7·05	0·7	99·3
	6·0	6·0	0·0	100·0

It will be observed that the above results do not altogether agree with those of Kopfer. It is plain that, with an amount of acid just a little more than what is required to neutralise all the free lime, a distillate is obtained which is a moderately concentrated solution of almost pure hypochlorous acid, and in this respect there is very little difference between the three acids employed; but (and here is the principal difference between our results and those of Kopfer) long before the amount of acid is sufficient to decompose the whole of the calcium hypochlorite theoretically present in the solution (see p. 445), the proportion of hypochlorous acid has fallen to about three-quarters of its original amount, and considerable quantities of chlorine have begun to be evolved. After the point at which all the hypochlorite theoretically present is decomposed, there is, as would be expected, a rapid drop in the amount of the hypochlorous acid produced, and this drop is more rapid in the case of the hydrochloric acid than with the other acids, because immediately there is an excess of hydrochloric acid it decomposes some of the hypochlorous acid, whereas the other acids have first to liberate some hydrochloric acid from the calcium chloride present.

The curves in Fig. 1 represent the action of the three acids already described. The point where two of them are almost horizontal, and in the other an actual rise in the proportion of hypochlorous acid is shown, is very near where the amount of acid is just sufficient to neutralise all the free lime and to decompose all the hypochlorite present.

FIG. 1.



Continuous curve ——— H_2SO_4.
Broken ,, - - - - - - HCl.
Dotted ,, ... HNO_3.

TABLE IV.

Distillation with Acetic Acid.

Volume of *N*-acid, in c.c.	Arsenite oxidised.	Chloride produced.	Hypochlorous acid, per cent.	Chlorine, per cent.
20	0·0	0·0	—	—
30	0·0	0·0	—	—
40	0·8	0·35	100·0	0·0
50	8·35	4·15	100·0	0·0
60	11·5	5·95	93·3	6·7
	11·5	5·9	94·9	5·1

TABLE IV (*continued*).

Distillation with Acetic Acid.

Volume of *N*-acid, in c.c.	Arsenite oxidised.	Chloride produced.	Hypo-chlorous acid, per cent.	Chlorine per cent.
70	15·3	8·1	88·9	11·1
	14·75	7·8	89·1	10·9
80	18·8	10·45	79·9	20·1
	18·1	10·0	81·0	19·0
90	21·1	12·35	70·8	29·2
	20·45	11·95	71·1	28·9
100	22·9	13·4	70·9	29·1
	23·9	14·0	70·7	29·3
120	25·35	14·45	75·4	24·6
	25·45	15·15	68·0	32·0
	26·0	15·1	72·2	27·8
140	25·6	15·9	61·0	39·0
	25·6	15·7	63·0	37·0
150	25·4	15·8	60·8	39·2
	25·8	15·8	63·3	36·7
170	25·0	15·7	59·2	40·8
	25·55	15·5	64·8	35·2
200	24·5	15·3	60·1	39·9
	24·5	15·5	58·1	41·9
250	22·5	15·05	49·5	50·5
	23·1	15·25	51·5	48·5
	20·8	13·55	53·5	46·5

TABLE V.

Distillation with Phosphoric Acid.

Volume of *N*-acid, in c.c.	Arsenite oxidised.	Chloride produced.	Hypo-chlorous acid, per cent.	Chlorine per cent.
40	3·4	1·65	100·0	0·0
50	11·35	5·85	94·0	6·0
	9·4	4·9	91·8	8·2
60	15·8	8·8	79·5	20·5
	15·55	8·55	81·9	19·1
70	21·0	12·25	71·4	28·6
	21·0	12·25	71·4	28·6
80	24·85	14·65	69·6	30·4
	26·45	15·6	69·6	30·4
90	32·7	19·1	71·2	28·8
	30·5	17·75	71·3	28·7
100	32·85	19·4	69·3	30·7
	34·05	20·2	68·6	31·4
120	33·25	20·3	63·8	36·2
	32·0	19·75	62·0	38·0
140	29·15	18·5	57·6	42·4
	30·15	19·0	58·7	41·3

TABLE V (*continued*).

Distillation with Phosphoric Acid.

Volume of *N*-acid, in c.c.	Arsenite oxidised.	Chloride produced.	Hypochlorous acid, per cent.	Chlorine per cent.
150	29·4	18·75	56·8	43·2
	30·0	19·2	56·2	43·8
170	24·45	15·95	53·3	46·7
	27·2	17·2	58·1	41·9
200	24·95	16·35	52·6	47·4
250	21·6	14·2	52·1	47·9
	21·9	14·9	47·0	53·0

The action of acetic and phosphoric acids is evidently very different from that of the stronger acids. As with those, when the amount of acid is only a little more than is required to neutralise the free lime, the distillate is almost pure hypochlorous acid, although in the case of acetic acid it is considerably weaker. As the amount of acid is increased, also, free chlorine begins to be evolved long before the acid is sufficient to decompose the whole of the hypochlorite present. The diminution in the amount of hypochlorous acid proceeds much more slowly than in the case of the stronger acids, and even with so large an amount of acid as 250 c.c. the amount of hypochlorous acid in the distillate does not fall much below 50 per cent.

The curves in Fig. 2 represent the action of acetic and phosphoric acids. As in Fig. 1, the point where the acid is just about sufficient to neutralise the free lime and to decompose all the hypochlorite present is plainly indicated.

The Action of Boric Acid on Bleaching Powder.

A Convenient Method of Preparing a Solution of Hypochlorous Acid.

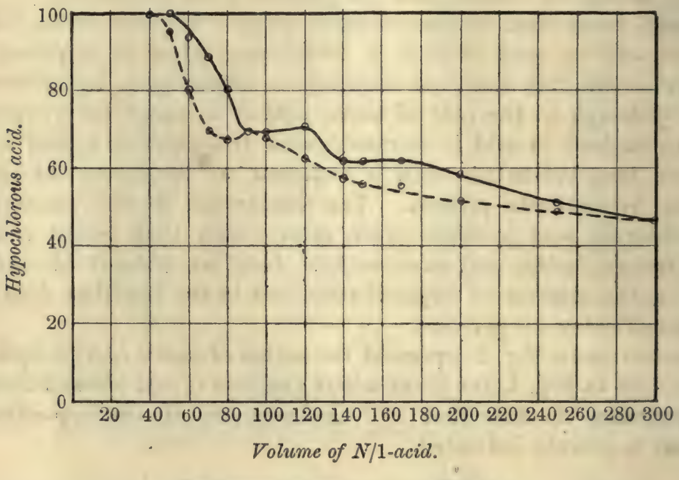
It is known that boric acid liberates hypochlorous acid from bleaching powder. Lauch (*Ber.*, 1885, **18**, 2287) took advantage of this for the preparation of some additive compounds of hypochlorous acid.

Of the two constituents of bleaching powder, boric acid appears to be only able to decompose to any considerable extent one of them—the calcium hypochlorite; so that, when bleaching powder is distilled with boric acid, there is never much free chlorine produced, and there is no difficulty in obtaining practically pure solutions of hypochlorous acid.

The best conditions for this purpose appear to be to distil the bleaching powder with about thirty times its weight of water and twice its weight of boric acid. So long as this proportion of water is maintained, it makes very little difference as to the amount of boric acid employed; it may even be increased to three times the weight of the bleaching powder. If, however, much less water is used, more free chlorine is produced.

If 10 grams of bleaching powder are distilled with 300 c.c. of water and any amount from 15 to 20 grams of boric acid, from 50 to 100 c.c. may be distilled off, and this will be a practically pure solution of hypochlorous acid, giving only a slight immediate turbidity with silver nitrate. This appears to us to be the simplest method of obtaining a solution of hypochlorous acid, as any ordinary variation in the proportions of acid and bleaching powder makes little difference in the result, so long as a sufficient amount of water is used, and there is not the difficulty of trying to avoid local excess of acid such as occurs when the stronger acids are employed.

FIG. 2.



Continuous curve ———— $C_2H_4O_2$.
Broken ,, - - - - - H_3PO_4.

The solution of hypochlorous acid so prepared is usually from 1·5 to 2N/10, and contains from 4 to 5 grams of pure hypochlorous acid per litre.*

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* Investigations on the bleaching and other properties of a solution of hypochlorous acid are in progress, the results of which will be communicated later.

The Action of Carbonic Acid on Bleaching Powder.

In the former paper already referred to (*loc. cit.*) it was demonstrated that, as had been stated by other observers (Wolters, *J. pr. Chem.*, 1874, [ii], **10**, 128; Lunge and Schäppi, *Dingl. Polyt. J.*, 1889, **273**, 63; Dreyfus, *Bull. Soc. chim.*, 1884, [ii], **41**, 600; von Tiesenholt, *J. pr. Chem.*, 1902, [ii], **65**, 512, and 1906, [ii], **73**, 301), when carbon dioxide is passed through a solution of bleaching powder, or over the moist solid substance, no hypochlorous acid is evolved, but only free chlorine. At first sight it appears remarkable that there should be such a wide difference between the action of two such weak acids as boric and carbonic acids as is indicated by the results described above. It must be borne in mind, however, that the conditions under which the two acids were experimented with were widely different, particularly as regards temperature, and we find that, under similar conditions, carbon dioxide acts practically in the same way as boric acid. If carbon dioxide is passed through a solution of bleaching powder which is kept boiling continuously, almost pure hypochlorous acid is given off. The experiment succeeds best if the carbon dioxide is bubbled fairly rapidly through the mixture of bleaching powder and water (in the same proportion as used in all the other experiments, namely, 10 grams of bleaching powder to 300 c.c. of water) from the beginning, whilst the liquid is being heated, and then the distillate collected as soon as the liquid boils vigorously. The yield of hypochlorous acid is not nearly so good if the liquid is heated first, and the carbon dioxide led in as soon as it boils. Doubtless the reason for this difference is that, when the carbon dioxide is bubbling through whilst the liquid is being heated, it is gradually removing the free lime, so that it is free to act on the calcium hypochlorite by the time the liquid is boiling.

The effect of passing carbon dioxide through a mixture of bleaching powder and water at different temperatures was tried, with the results given in table VI.

In each experiment the mixture of 10 grams of bleaching powder and 300 c.c. of water was heated in a flask to the desired temperature. The carbon dioxide was freed from hydrochloric acid by passing it over wet glass wool. It was not passed through from the commencement, but only when the desired temperature was reached. The resulting gases were passed through 25 c.c. of $N/10$-arsenite, and the proportions of hypochlorous acid and chlorine determined in the usual way.

TABLE VI.

Temperature of mixture.	Arsenite oxidised.	Chloride produced.	Hypochlorous acid, per cent.	Chlorine, per cent.
30°	8·75	8·3	5·3	94·7
40	10·4	9·0	15·5	84·5
50	10·2	8·75	16·6	83·4
60	8·95	7·4	20·9	79·1
70	10·25	7·35	39·4	60·6
80	11·45	8·05	42·2	57·8
90	10·6	6·7	58·2	41·8
100	10·3	5·4	90·7	9·3

As will be seen from the table, hypochlorous acid (mixed with a large proportion of free chlorine) begins to come off as soon as the liquid becomes warm, and the proportion steadily increases as the temperature rises, until when the liquid is at 100° almost pure hypochlorous acid is evolved. (In the experiment at 100° the liquid was kept as nearly as possible at that temperature. Not being pure water it did not absolutely boil. As pointed out above, if the liquid is kept actively boiling all the time the carbon dioxide is passing through, practically pure hypochlorous acid is evolved.)

We venture to submit that this remarkable difference in the action of carbonic acid at different temperatures affords strong evidence in favour of Taylor's view that the action of carbonic acid on bleaching powder in the cold is the same as that of other acids, the carbonic acid decomposing both the calcium chloride and the hypochlorite, and the resulting hydrochloric and hypochlorous acids decomposing each other, with the liberation of chlorine. The solubility of carbon dioxide in water diminishes as the temperature rises, and at the boiling point of water it is practically nil, so that at that temperature the amount of true carbonic acid (H_2CO_3) present must be almost infinitesimal. Consequently, at the higher temperature it, like boric acid, can only decompose the calcium hypochlorite in the bleaching powder, with the result that pure hypochlorous acid is evolved. Further (and this, of course, is of some importance), whilst the liquid is actually boiling, the hypochlorous acid is removed from it practically as fast as it is produced. The results of our experiments at different temperatures, as expressed in table VI, indicate the gradually diminishing amount of true carbonic acid which can exist in the water as the temperature rises, and the solubility of the carbon dioxide diminishes.

The removal of the hypochlorous acid from the solution as fast as it is produced is also an important factor in the action of boric acid on bleaching powder. As described above, when bleaching powder solution is boiled with boric acid, pure hypochlorous acid is driven off, but the action is very different at the ordinary temperature.

In the following experiments 3 grams of bleaching powder were rubbed with 100 c.c. of water, and 6 grams of boric acid added. Through this mixture air, free from carbon dioxide, was bubbled, and the issuing gases were passed through *N*/10-arsenite, with the following results:

	Arsenite oxidised.	Chloride produced.	Hypochlorous acid, per cent.	Chlorine, per cent.
1.	5·0	3·76	33	67
2.	6·35	4·67	36	64

The experiments took about twenty-four hours to produce the observed amount of oxidation in the arsenite. This means that the action is very slow as compared with the action of carbon dioxide at the ordinary temperature. This, together with the fact that not pure chlorine, but a mixture of chlorine and hypochlorous acid, is evolved, leads us to the conclusion that boric acid at the ordinary temperature does not act on bleaching powder in the same way as carbonic acid and other acids. The slow evolution of chlorine we attribute to the fact that the boric acid simply unites with the free lime, and so enables the reverse action to proceed, as described in the former paper (*loc. cit.*, p. 2550). The hypochlorous acid which accompanies the chlorine is doubtless due to the action of the boric acid on the calcium hypochlorite in the solution. (It must be borne in mind that, in all experiments where chlorine and hypochlorous acid are swept out by passing air through a liquid, the chlorine, being much less soluble in water, will be swept out more readily, so that the proportion of hypochlorous acid actually present in the liquid is certainly greater than the numbers indicate.)

The results of the above two experiments are somewhat similar to those in table VIII in the former paper (p. 2551), which were obtained by passing air, free from carbon dioxide, through a solution of bleaching powder which had been first exposed to air in order to remove the free lime. The addition of boric acid, even in considerable quantity, is simply equivalent to exposing the bleaching powder solution to air for some time; there is apparently no action of the boric acid on the calcium chloride in the solution.

It is hardly necessary to point out that if any other acid be added to bleaching powder solution in quantity just sufficient to unite with the free lime, the effect of afterwards passing air free from carbon dioxide through the solution will be similar to what is described above. Experiments were made with hydrochloric and nitric acid. With the former the air free from carbon dioxide swept out a mixture of 85 per cent. of chlorine and 15 per cent. of hypochlorous acid, and with the latter 75 per cent. of chlorine and 25 per cent. of hypochlorous acid. One would expect the proportion of chlorine to be greater with hydrochloric acid than with nitric, because if in adding the acid to the bleaching powder solution there is at any time a local excess of acid, the former is more likely to produce free chlorine than the latter.

Summary.

(1) When bleaching powder, mixed with thirty times its weight of water, is distilled with sulphuric, hydrochloric, or nitric acid in quantity slightly greater than is required to neutralise the free lime present, hypochlorous acid mixed with a small quantity of free chlorine is evolved. When the acid is in sufficient quantity to neutralise all the free lime and to decompose the whole of the hypochlorite theoretically present, the proportion of free chlorine is considerably greater. When the amount of acid is further increased, the hypochlorous acid produced rapidly diminishes, and very soon nothing but chlorine is evolved. There is not a great difference in the action of the three acids named.

(2) Acetic and phosphoric acids behave much alike, but they differ considerably, as would be anticipated, from the three acids above mentioned. Even with comparatively large amounts of these acids the proportion of hypochlorous acid evolved does not fall much below 50 per cent.

(3) When bleaching powder is distilled with boric acid and a sufficient amount of water, almost pure hypochlorous acid is produced, and there is very little difference in the result if the boric acid used is as much as three times the weight of the bleaching powder. This is recommended as a convenient method of preparing a solution of hypochlorous acid.

(4) When carbon dioxide is bubbled through a mixture of bleaching powder and water at different temperatures, whilst at the ordinary temperature nothing but chlorine is evolved, as soon as the liquid becomes warm hypochlorous acid begins to come off. The proportion of hypochlorous acid increases as the temperature rises, and when the liquid boils it is practically pure, hardly any free chlorine being evolved. It is suggested that this is strong evidence in favour of Taylor's view that the action of carbonic acid on bleaching powder at the ordinary temperature is like that of other acids.

(5) When boric acid is added to a solution of bleaching powder, and air free from carbon dioxide is passed through at the ordinary

temperature, a mixture of chlorine and hypochlorous acid is swept out, containing a considerable excess of the former. The boric acid simply unites with the free lime, and this allows the reverse action to proceed, free chlorine being produced. If any other acid is added to a solution of bleaching powder in quantity just sufficient to neutralise the free lime, the passing of air free from carbon dioxide through the solution gives a similar result.

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LV.—*The Influence of Three- and Four-membered Carbon Rings on the Refractive and Dispersive Power of Organic Compounds.*

By GUSTAF JIM ÖSTLING.

DURING the course of his spectrochemical researches, Brühl stated that ring-formation has no influence on the molecular refractive power, at all events in the case of the cyclic compounds which he examined, and although he found slightly higher values than those calculated in the ordinary way for some *cyclo*propane and *cyclo*butane compounds, he seems to have attributed these chiefly to experimental errors (*Ber.*, 1899, **32**, 1222). Tschugaeff later (*Ber.*, 1900, **33**, 3122), in the case of the tanacetone compounds, observed a constant increment for the molecular refraction amounting to +0·67. He assumed that this was due to the presence of a three-carbon ring in the molecule (compare also Aschan, "Chemie der alicyklischen Verbindungen," 1905, p. 281—282). As there are many optical measurements for *cyclo*propane compounds in the literature, which after recalculation seemed to indicate varying increments above those calculated in the usual manner, it appeared to the author that it would be interesting to investigate this subject more thoroughly, and to study also the *cyclo*butane derivatives. It seemed also probable that the measurements of the dispersive power, which in so many cases appear to be a valuable indication of difference of constitution, would give interesting results.

The determination of the refractive constants was made in a very accurate Pulfrich refractometer, the readings being taken twice at short intervals. The densities were determined with pyknometers (Ostwald and Sprengel), which were seldom smaller than of 2 c.c. capacity. The thermometers used were divided into 0·1°. The densities were always compared with that of water at 4°, and where this value was not given in the literature it was calculated. Where, as often happened, the density and the refractive index had not been determined at the same temperature, the density was reduced to the temperature of the refractive index with the usual difference of 0·0008 per degree.

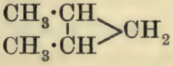
For the calculation of the molecular refraction the formula of Lorentz and Lorenz was employed, namely:

$$MR = \frac{n^2-1}{n^2+2} \times \frac{M}{d}.$$

The numbers recently calculated by Eisenlohr (*Zeitsch. physikal. Chem.*, 1910, **75**, 585) for the atomic refraction were used for obtaining the theoretical values.

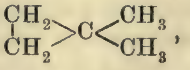
Among the *cyclo*propane compounds employed, tanacetone and its reduction product, tanacetyl alcohol, may first be mentioned, and next the methyl esters of the oxidation products, α-thujaketonic acid and α-tanacetonedicarboxylic acid. Professor L. Tschugaeff also kindly supplied the author with pure samples of α-thujene and of thujane (*Compt. rend.*, 1910, **151**, 1058).

A new hydrocarbon of the *cyclo*propane series was prepared, namely, 1:2-*dimethyl*cyclo*propane*,



$$\left.\begin{array}{l}CH_3\cdot CH\\ \quad\ \ | \\ CH_3\cdot CH\end{array}\right\rangle CH_2$$

from βδ-dibromopentane by treatment with zinc and alcohol.* This hydrocarbon is stable towards permanganate at first, but the colour begins to weaken two minutes after adding the permanganate, and disappears five to ten minutes later.† It is very unstable towards bromine, with which it reacts violently at −2°. In this respect its behaviour is similar to that of 1:1-dimethyl*cyclo*propane,



$$\left.\begin{array}{l}CH_2\\ | \\ CH_2\end{array}\right\rangle C\left\langle\begin{array}{l}CH_3\\ CH_3\end{array}\right.,$$

which according to Gustavson and Popper (*J. pr. Chem.*, 1898, [ii], **58**, 458) also combines energetically with bromine, giving αγ-dibromo-ββ-dimethylpropane. It has also been observed (Demjanoff, *Ber.*, 1895, **21**, 22) that methyl*cyclo*propane unites more readily in the dark with bromine than does *cyclo*propane, but in the case of methyl*cyclo*propane violent reaction only takes place in sunlight, whereas both the dimethyl*cyclo*propanes, even in diffused light, react very violently with bromine. This is also the case with 1 : 2 : 3-trimethyl*cyclo*propane. A similar decrease in the stability of the ring on substitution with methyl groups is also to be seen in the case of some of the mono-, di-, and tri-carboxylic acids of *cyclo*propane (compare Kötz, *J. pr. Chem.*, 1907, [ii], **75**, 433).

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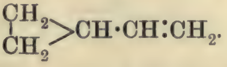
* The same hydrocarbon has been quite recently prepared by Zelinsky and Ujedinoff (*J. pr. Chem.*, 1911, [ii], **84**, 573). The properties are in accordance with those mentioned here, except as regards the behaviour with bromine.

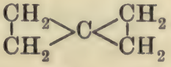
† Baeyer's test was always so carried out that two to three drops of the substance were shaken with about 2 c.c. of 2 per cent. sodium carbonate solution, and then a drop of 1 per cent. permanganate solution added.

The next substance to be examined was the hydrocarbon first obtained by Gustavson (*J. pr. Chem.*, 1896, [ii], **54**, 99) from pentaerythritol tetrabromohydrin by the action of zinc and alcohol, and which he called vinyl*cyclo*propane,



$$\left.\begin{matrix}CH_2\\|\\CH_2\end{matrix}\right> CH\cdot CH{:}CH_2.$$

Fecht (*Ber.*, 1907, **40**, 3883) later assigned the structure



$$\left.\begin{matrix}CH_2\\|\\CH_2\end{matrix}\right> C \left<\begin{matrix}CH_2\\|\\CH_2\end{matrix}\right.$$

to the hydrocarbon, and named it *spiro*pentane. Whilst they do not definitely settle the question, the spectrochemical numbers are in favour of Gustavson's formula (compare table I and p. 476).

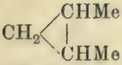
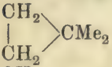
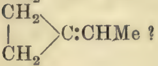
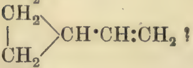
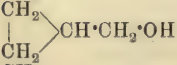
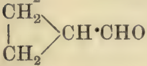
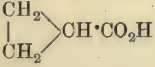
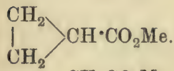
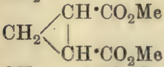
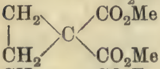
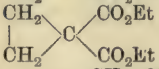
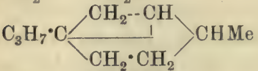
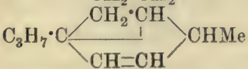
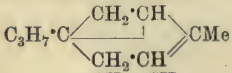
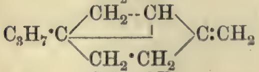
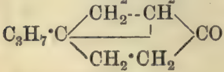
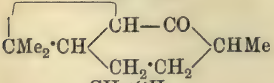
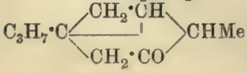
The esters of various *cyclo*propanecarboxylic acids have also been studied.

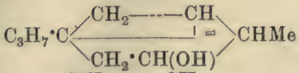
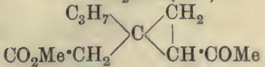
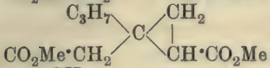
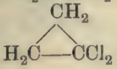
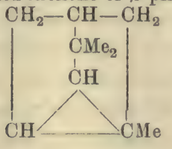
Two tricyclic terpenes were also used for the purpose of this research, namely, cyclene (tricyclene) and β-pinolene or *cyclo*fenchene (*Annalen*, 1912, **387**, 1), specimens of which were kindly supplied by Professor O. Aschan. Both these terpenes contain a *cyclo*propane ring.

The results of the measurements of the *cyclo*propane compounds are summarised in table I. The first four columns give the constitutional formulæ of the substances, boiling points, the densities, and the corresponding temperatures respectively; the next two columns give the differences between the experimental and the theoretical values for molecular refraction for the hydrogen line C and for the sodium line D, whilst the last column indicates the difference between the experimental and the theoretical values for molecular dispersion between the two hydrogen lines C and G.

In those cases where the numbers are taken from the literature, references are given.

TABLE I.

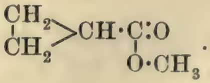
					Increment for		
No.	Formula.	B. p.	D^t_4.	t.	M_α.	M_D.	$M_\gamma - M_\alpha$.
1		32·6–33·2°/ 761 mm.	0·6755	22·2°	+0·68	+0·68	+0·05
2		21° 21	0·6604 0·6619	20·0 17·0	— —	+0·67 +0·77	—[3] —[4]
3		37·5°/750 mm.	0·7052	18·0	—	+0·92	—[5]
4		42–42·8°/ 755 mm. 40°	0·7375 0·7237	16·0 18·0	+0·71 --	+0·75 +0·82	+0·08 =11 % —[5]
5		123·2–123·4° /738 mm.	0·8995	17·5	—	+0·71	—[6]
6		98°/737 mm.	0·9294	17·6	—	+0·90	—[6]
7		181–182·5° 183·2–184°	1·0907 1·0897	17·1 19·7	+0·65 +0·67	+0·67 +0·68	+0·06 =12 %[1] +0·07 =14 %
8		119°/764 mm.	0·9848	20·1	+0·63	+0·66	+0·07 =10 %
9		219–220°/ 764 mm.	1·1584	15·9	+0·77	+0·81	+0·09 =10 %
10		196·6–196·7° /748 mm.	1·1509	15·75	+0·65	+0·71	+0·08 =9 %
11		214–215°/ 760 mm.	1·0624	19·1	+0·71	+0·74	+0·11 =10 %
12		156·2–156·8° /756 mm.	0·8142	19·5	+0·69	+0·70	+0·04
13		150–151°/ 750 mm.	0·8232	22·0	—	+0·78	—[8]
14		152–152·5° 151–152°/ 755 mm.	0·8275 0·8294	20·0 17·4	— +0·65	+0·72 +0·67	—[8] +0·07 =6 %
15		163–165°/ 757·6 mm.	0·8422	17·0	+1·33	+1·36	+0·23[9] =19 %
16		95·4–95·6°/ 15 mm.	0·9556	19·3	+0·89	+0·92	+0·12 =12 %[7]
17		99–100°/ 15 mm.	0·9577	18·8	+0·99	+1·03	+0·12 =11 %[1]
18		201–202°/ 760 mm.	0·9193 0·9182	15·1 17·6	+0·72 +0·70	+0·76 +0·70	+0·02 +0·01[1]

No.	Formula.	B. p.	D^t_4.	t.	Increment for M_α.	M_D.	$M_\gamma - M_\alpha$.
19		209·8–210·1 /757 mm.	0·9202	19·1	*+0·58*	*+0·62*	*+0·04*
20	 ...	—	1·0126	18·1	*+0·70*	*+0·73*	*+0·08* =6 %
21	 ...	126–127°/ 12 mm.	1·0535	18·9	*+0·62*	*+0·64*	*+0·08* =6 %
22		75–76°	1·2105	17·7	*+0·55*	*+0·56*	*+0·03*[10]
23	Cyclene, $C_{10}H_{16}$ (tricyclic)	152·5°/747 mm.	0·8268	80·2	*+0·88*	—	*+0·05*[2]
		152°/740 mm.	0·8440	66·0	*+0·77*	*+0·80*	(*−0·05*)
24	β-Bornylene, $C_{10}H_{16}$ (tricyclic).	—	0·7948	120·8	*+0·81*	—	*+0·07*[2]
25	*cyclo*Fenchene or β-pinolene, 	144°/770 mm.	0·8624	16·2	*+0·89*	*+0·95*	*+0·07*

[1] Brühl, *Ber.*, 1899, **32**, 1222.
[2] Eykman, *Chem. Weekblad*, 1906, **3**, 653, 685, 701 ; 1907, **4**, 41.
[3] Gustavson and Popper, *J. pr. Chem.*, 1898, [ii], **58**, 458.
[4] Gustavson, *ibid.*, 1900, [ii], **62**, 271.
[5] Gustavson, *ibid.*, 1896, [ii], **54**, 105.
[6] Demjanoff and Fortunatoff, *Ber.*, 1907, **40**, 4397.
[7] K. Auwers (private communication).
[8] Tschugaeff, *Ber.*, 1904, **37**, 1482.
[9] Auwers, Roth, and Eisenlohr, *Annalen*, 1910, **373**, 249.
[10] Brühl, *Ber.*, 1892, **25**, 1954.

It will be noticed from table I that the increments for M_α and M_D are approximately +0·7, but in a few cases the values are somewhat higher. The highest value is that of sabinene (No. 15) with the increments +1·33 and +1·36. This substance contains a semicyclic double linking, and this tends to increase the molecular refraction. The values for Nos. 6, 16, and 17 are also high. In these cases the three-carbon ring is conjugated with a double bond, namely, a carbonyl group. The determinations for carone and sabinaketone were made with pure substances and with great accuracy; thus this increase in refractive power undoubtedly corresponds with the similar increase in the case of compounds containing conjugated ethylene linkings or one ethylene linking and one carbonyl linking.

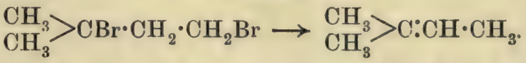
In the ethereal salts of the *cyclo*propanecarboxylic acids the *cyclo*propane ring is also conjugated with a carbonyl group. Here the conjugation is influenced by the presence of an alkyloxy-group, thus:



$$\left.\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}\right>CH\cdot\underset{\displaystyle O\cdot CH_3}{\underset{|}{C}}:O\ .$$

It is known (Auwers and Eisenlohr, *J. pr. Chem.*, 1910, [ii], **82**, 65) that in the case of conjugated double linkings an alkyl or alkyloxy-group substituted at one of the central carbon atoms greatly lowers the increment. It is therefore not surprising that the small increment, which might be expected to be caused by the conjugation between the *cyclo*propane ring and the double bond, in these cases totally vanishes.

Here the fact may be mentioned that both the dimethyl*cyclo*propanes synthetised by Zelinsky and Zelikoff (*Ber.*, 1901, **34**, 2862) give increments for molecular refraction which are considerably higher than those noticed in other similar cases. One of them, namely, 1:1:2-trimethyl*cyclo*propane, was prepared according to Zelinsky's directions, and obtained with practically the same boiling point, density, and refractive index. As this hydrocarbon, however, unlike all other *cyclo*propane compounds, instantly decolorises potassium permanganate, also since in no other case has a *cyclo*propane derivative resulted from a tertiary bromide by the action of zinc and alcohol, its constitution is doubtful. It should also be mentioned here that Ipatieff (*J. Russ. Phys. Chem. Soc.*, 1890, **30**, 292) obtained from $\alpha\gamma$-dibromo*iso*pentane, trimethylethylene, but no *cyclo*propane derivative:



$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right>CBr\cdot CH_2\cdot CH_2Br \longrightarrow \left.\begin{matrix}CH_3\\CH_3\end{matrix}\right>C:CH\cdot CH_3.$$

Lastly, the above so-called trimethyl*cyclo*propane of Zelinsky exhibits a value for dispersion 20 per cent. higher than that calculated on the basis of its being a *cyclo*propane derivative.

Against the constitution of Zelinsky and Zelikoff's 1:2:3-trimethyl*cyclo*propane (*loc. cit.*) nothing can be said, especially as this hydrocarbon is stated to be stable towards permanganate. The value for the molecular refraction obtained from the numbers given by these chemists is 29·08, whereas C_6H_{12} requires 27·71. The increment caused by the three-carbon ring-formation is therefore in this case 1·37. Whatever the reason may be for this unusually high value, it has been omitted in calculating the quantitative influence of the *cyclo*propane ring on molecular refraction.

If we next examine the values for dispersion in table I, we may first consider those compounds in which there is no conjugation of the three-carbon ring with a double linking, namely:

	$\Delta M_{\gamma}-M_{\alpha}$.		$\Delta M_{\gamma}-M_{\alpha}$.
1 : 2-Dimethyl*cyclo*propane	+0·05	β-Pinolene	+0·07
Dichloro*cyclo*propane	+0·03	Cyclene	+0·05
Thujane	+0·04	β-Bornylene	+0·07
Tanacetyl alcohol	+0·04		

The differences are not greater than the possible error of experiment. The fact that the differences are all positive seems, however, to indicate a slight influence, but that is, in any case, very small when compared with the increment caused by the ethylene linking (+0·20).

If we now consider:

	$\Delta M_{\gamma}-M_{\alpha}$.
Sabinene	+0·23 = 19% increment
Sabinaketone	+0·12 = 12 ,,
Carone	+0·12 = 11 ,,

we find a marked increase in the dispersion. Auwers and Ellinger (*Annalen*, 1912, **387**, 200) have recently shown that hydrocarbons with only one semicyclic ethylene linking exhibit an average increment of 7—8 per cent. above that calculated for dispersion, and for refraction $E\Sigma_D = +0{\cdot}4$. Allowing for the presence of the semicyclic double bond in sabinene, we thus find that the increments for the dispersion in the case of the three compounds are practically the same. The esters of the *cyclo*propanecarboxylic acids give also dispersion increments of about the same value (compare table I), showing that the substitution of an alkyloxy-group does not affect the dispersion so much as it does the refraction.

The conjugation of a *cyclo*propane and a double linking produces, therefore, an increment for the molecular dispersion of approximately 10 per cent.

We may now turn to the *cyclo*butane compounds, the results of the measurements of which are given in table II, this being drawn up on the same principle as table I.

TABLE II.

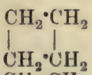
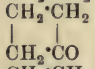
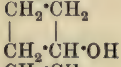
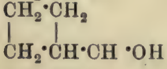
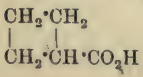
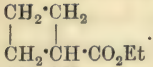
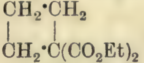
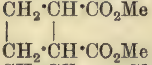
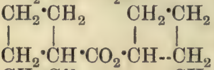
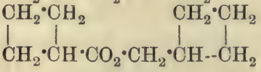
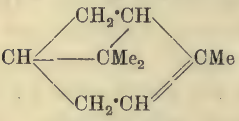
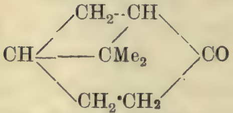
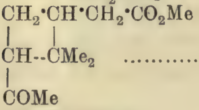
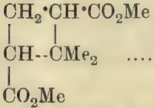
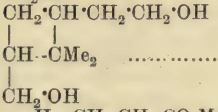
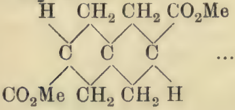
					Increment for		
No.	Formula.	B. p.	D^{t}_{4}.	*t*.	M_{α}.	M_{D}.	$M_{\gamma}-M_{\alpha}$.
1		10—11°/ 726 mm.	0·703	0·0°	—	*−0·21*	— [1]
2		98·5—99°/ 745 mm.	0·9381	16·0	—	*+0·49*	— [2]
3		123°/ 740 mm.	0·9159	20·0	—	*+0·42*	— [3]
4		143—144°/ 760 mm.	0·9127	8·7	*+0·52*	*+0·53*	*+0·02* [5]
			0·9113	20·0	—	*+0·51*	— [6]
5		195—195·6°/ 759 mm.	1·0577	18·1	*+0·47*	*+0·49*	*+0·04*
		195°/ 760 mm.	1·0570	16·6	*+0·46*	*+0·46*	*−0·02* [7]

TABLE II (*continued*).

No.	Formula.	B. p.	D_4^t.	*t*.	Increment for			
					M_α.	M_D.	$M_\gamma - M_\alpha$.	
6	 $\begin{array}{l} CH_2\cdot CH_2 \\ \vert \qquad \vert \\ CH_2\cdot CH\cdot CO_2Et \end{array}$	157°/ 750mm.	0·9525	19·85	*+0·40*	*+0·43*	*+0·03*	
7	 $\begin{array}{l} CH_2\cdot CH_2 \\ \vert \qquad \vert \\ CH_2\cdot C(CO_2Et)_2 \end{array}$	104—105°/ 12 mm.	1·0456	20·0	—	*+0·37*	—	[3]
8	 $\begin{array}{l} CH_2\cdot CH\cdot CO_2Me \\ \vert \qquad \vert \\ CH_2\cdot CH\cdot CO_2Me \end{array}$	114—114·5°/ 20 mm.	1·1191	17·3	*+0·52*	*+0·54*	*+0·03*	
9	 $\begin{array}{l} CH_2\cdot CH_2 \qquad CH_2\cdot CH_2 \\ \vert \qquad \vert \qquad\qquad \vert \qquad \vert \\ CH_2\cdot CH\cdot CO_2\cdot CH\text{--}CH_2 \end{array}$	198·5—199°/ 750 mm.	0·9991	19·0	—	*+0·84*	—	[4]
10	 $\begin{array}{l} CH_2\cdot CH_2 \qquad\qquad CH_2\cdot CH_2 \\ \vert \qquad \vert \qquad\qquad\qquad \vert \qquad \vert \\ CH_2\cdot CH\cdot CO_2\cdot CH_2\cdot CH\text{--}CH_2 \end{array}$	218—220°/	0·9779	19·0	—	*+0·97*	—	[6]
11		— *d*, α-156·4—156·6°/ 757 mm.	0·8635 0·8594	16·2 18·05	*+0·46* *+0·37*	— *+0·46*	*+0·07* *+0·05*	[8] [9]
12		118·2°/ 43 mm.	0·9827	14·65	*+0·51*	*+0·57*	*+0·06*	
13	 $\begin{array}{l} CH_2\cdot CH\cdot CH_2\cdot CO_2Me \\ \vert \qquad \vert \\ CH\text{--}CMe_2 \\ \vert \\ COMe \end{array}$	254—255°/ 755 mm.	1·0187	15·2	*+0·40*	*+0·44*	*+0·05*	
14	 $\begin{array}{l} CH_2\cdot CH\cdot CO_2Me \\ \vert \qquad \vert \\ CH\text{--}CMe_2 \\ \vert \\ CO_2Me \end{array}$	228—229°/ 756 mm. 113—113·8°/ 11 mm.	1·0694	13·7	*+0·44*	*+0·48*	*+0·04*	
15	 $\begin{array}{l} CH_2\cdot CH\cdot CH_2\cdot CH_2\cdot OH \\ \vert \qquad \vert \\ CH\text{--}CMe_2 \\ \vert \\ CH_2\cdot OH \end{array}$	166—167°/ 17 mm.	0·9947	19·8	*+0·28*	*+0·31*	*+0·03*	
16		149°/ 18 mm.	1·0982	20·1	*+1·12*	*+1·14*	*+0·06*	

[1] Willstätter, *Ber.*, 1907, **40**, 3982.

[2] Kijner, *J. Russ. Phys. Chem. Soc.*, 1905, **37**, 106.

[3] Zelinsky and Gutt, *Ber.*, 1907, **40**, 4744.

[4] Demjanoff and Dojarenko, *ibid.*, 2954.

[5] W. H. Perkin, sen., Trans., 1901, **79**, 331.

[6] Demjanoff, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 837.

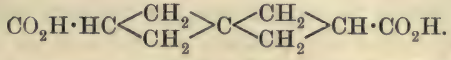
[7] Brühl, *Ber.*, 1899, **32**, 1222.

[8] Eykman, *Chem. Weekblad*, 1906, **3**, 653, 685, 701; 1907, **4**, 41.

[9] Auwers, Roth, and Eisenlohr, *Annalen*, 1910, **373**, 274.

The author has here to thank Professor W. H. Perkin for supplying several valuable *cyclo*butane compounds, such as nopinone, *cyclo*butanecarboxylic acid, and others.

The methyl ester of *spiro*heptanedicarboxylic acid was also prepared and examined. Fecht (*loc. cit.*) assigned to this acid the formula:



$$CO_2H\cdot HC{<}{\substack{CH_2\\CH_2}}{>}C{<}{\substack{CH_2\\CH_2}}{>}CH\cdot CO_2H.$$

The author has again verified the formula by the analysis of the acid and of its ester. The heat of combustion has also been determined, and agrees with the above view of its constitution.

Except in the case of *cyclo*butane itself we find in table II a far greater uniformity than in the case of the *cyclo*propane derivatives. Nopinone, which in its structure corresponds with sabinaketone, has a slightly higher increment than the others. It may be that here also the conjugation of a *cyclo*butane ring with a carbonyl group is the cause of the higher increment. The substance was quite pure, and the whole quantity (about 60 grams) had a constant boiling point. *cyclo*Butane compounds in general exhibit a slightly higher value for the molecular dispersion than that calculated, but here again the increments are scarcely larger than the possible error of experiment.

The results of this investigation show that:

(I) The closing of the *cyclo*propane ring as well as of the *cyclo*butane ring brings about an increase in the molecular refraction.

The increment in the case of the *cyclo*propane ring is for M_α +0·67 and for M_D +0·71; in the case of the *cyclo*butane ring for M_α +0·45 and for M_D +0·48.*

(II) A slightly higher value for refraction ($E\Sigma_D$ = about +0·2) is noticeable when the *cyclo*propane ring is conjugated with a double linking. This exaltation seems to disappear when an alkyl or an alkyloxy-group is attached to one of the central carbon atoms.

(III) The closing of the *cyclo*propane and *cyclo*butane rings has practically no influence on molecular dispersion.

(IV) The conjugation of a *cyclo*propane ring with a double linking increases the value of the molecular dispersion calculated for the two hydrogen lines *C* and *G* by approximately 10 per cent.

For comparison the dimethyl ester of *cyclo*pentane-1:2-dicarboxylic acid was also prepared and examined (see p. 475). Here the experimental and the theoretical values are in close agreement.

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* In calculating thus numerical values, numbers 3, 4, 6, 15, 16, 17, and 22 have for reasons already mentioned been omitted from table I., and similarly numbers 1, 7, 15, and 16 from table II.

This again is in accordance with many previous observations in the case of *cyclo*pentane and *cyclo*hexane compounds.

With regard to the influence of the closing of *cyclo*-heptane, -octane, and -nonane rings, so few substances of these classes have been prepared that it is not possible to draw any definite conclusions as to the influence of these ring-formations. Some measurements carried out by Willstätter and by Zelinsky seem to indicate that these ring-formations produce an increase in the molecular refraction.

Dr. T. M. Lowry kindly determined the magnetic rotation of β-pinolene, and found:

$$\frac{\text{Rotation of terpene, 20 cm.}}{\text{Rotation of water, \ \ 20 cm.}} = 1{\cdot}079$$

for both liquids at 20°.

The density determined after redistillation gave D^{20}_{20} 0·8608. The molecular magnetic rotation of β-pinolene calculated from these numbers is thus 9·478.

As this is the first time that the magnetic rotation of a compound containing three ring systems has been determined, it is interesting to notice the influence of ring-formations of various kinds on the magnetic rotation, a matter which has already been studied by W. H. Perkin, sen. (Trans., 1902, **81**, 292) in the case of mono- and bi-cyclic compounds.

For this purpose we may compare β-pinolene with some other isomeric terpenes, for which the magnetic rotation has been determined.

	Molecular magnetic rotation.	
$\Delta^{3:8(9)}$-*p*-Menthadiene	13·061	(conjugated double bonds)
d-Limonene	11·246	
l-Limonene	11·162	
Pinene	10·294	
β-Pinolene	9·478	

The difference between β-pinolene and the bicyclic terpene pinene is slightly less than that between the latter and both of the limonenes. It may be that this is due to the *cyclo*propane ring in the molecule of β-pinolene.

Perkin (*loc. cit.*) mentions that the two first members in the aliphatic series always show an abnormally high magnetic rotation, as, for example, in the case of acetic acid, and especially formic acid. The reason for this anomaly is somewhat obscure, but perhaps is due to the highly associated condition of the molecules of these acids. It seems, therefore, preferable to calculate the effect of ring-formation by the comparison of alicyclic compounds with aliphatic compounds containing the same number of carbon atoms in the molecule. The following values are thus obtained:

	Molecular magnetic rotation.	
Butyric acid	4·472	0·331
*cyclo*Propanecarboxylic acid	4·141	
Valeric acid	5·513	0·465
*cyclo*Butanecarboxylic acid	5·048	
Hexoic acid	6·530	0·639
*cyclo*Pentanecarboxylic acid	5·891	

From these few data naturally no definite quantitative influence of the *cyclo*propane ring on magnetic rotation can be deduced, but they indicate that the influence on the molecular magnetic rotation in the case of *cyclo*propane formation is different from that in the case of the formation of five- and six-membered carbon rings.

In most cases the magnetic rotation is more sensitive to constitutional influences than is the molecular refraction (compare, for example, the influence of conjugated double linkings). Here, with regard to the *cyclo*propane ring, the opposite seems to be the case. When two hydrogen atoms are removed by the formation of a five- or six-membered ring there is an alteration in the molecular refraction of $-2·2$, and by the formation of a *cyclo*propane ring of $-1·5$, and lastly, in the case of the double bond an alteration of $-0·5$. The corresponding numbers for the molecular magnetic rotation, $-0·6$, $-0·3$, and $+0·7$, show in the two last cases a relatively higher difference.

EXPERIMENTAL.

1 : 2-*Dimethyl*cyclo*propane.*

Pentane-$\beta\delta$-diol, $CH_3\cdot CH(OH)\cdot CH_2\cdot CH(OH)\cdot CH_3$, was first obtained by the reduction of acetylacetone with 3 per cent. sodium amalgam. The yield was unsatisfactory because a product of higher boiling point (pinacone formation) was obtained in about the same quantity as the glycol. The glycol boiled at 103—105°/14 mm. The other product boiled at 180—185°/14 mm., and solidified partly to very volatile, colourless crystals, melting at 77—78°.

The rest of the glycol needed for this experiment was obtained by reducing methyl β-hydroxypropyl ketone (Porai-Koschitz, *J. Russ. Phys. Chem. Soc.*, 1903, **35**, 1112) and the $\beta\delta$-dibromopentane obtained from it boiled at 71—72°/17 mm. (Found, Br = 68·4. Calc., Br = 69·56 per cent.)

After treating with zinc dust and alcohol (75 per cent.) and warming to about 60°, a hydrocarbon was obtained, which after redistillation over sodium boiled at 32·4—33·2°/761 mm. The hydrocarbon had a characteristic odour, and the yield was about 40 per cent. The following data were obtained:

$D_4^{22\cdot2}$ 0·6754 (hence $D_4^{19\cdot6}$ 0·6776).
n_α 1·37493, n_D 1·37665, n_β 1·38209, n_γ 1·38598 at 19·6°.

	M_α.	M_D.	$M_\beta - M_\alpha$.	$M_\gamma - M_\alpha$.
Found	23·67	23·77	0·40	0·62
Calc. for C_5H_{10}	22·99	23·09	0·36	0·57
Δ	+0·68	+0·68	+0·04	+0·05

A quantity of the hydrocarbon was dissolved in dry ether (10 per cent. solution), and, after cooling to 0°, bromine was added. A vigorous reaction ensued on the addition of each drop. Another part of the hydrocarbon was similarly dissolved in chloroform, and bromine added. As soon as the calculated amount of bromine had been used, the solution became more deeply coloured. The chloroform and ethereal solutions were united, and the dibromide obtained from them boiled at 78—82°/20 mm. It appears that the rupture of the ring takes place chiefly between the two methyl-substituted carbon atoms. This bromide gave, on treatment with zinc and alcohol, a product boiling at 32—34°, and having the characteristic odour of 1:2-dimethyl*cyclo*propane.

An attempt was also made to dissolve the hydrocarbon in a mixture of sulphuric acid (2 vols.) and water (1 vol.) at 0°, but it did not dissolve, even at the ordinary temperature.

1:1:2-*Trimethyl*cyclo*propane.*

In order to obtain diacetone alcohol, an attempt was first made to prepare it from diacetoneamine hydrogen oxalate (Zelinsky and Zelikoff, *loc. cit.*), but as the yield was very unsatisfactory the diacetone alcohol was later prepared by the following modification of Koelichens' method (*Zeitsch. physikal. Chem.*, 1900, **33**, 130).

Acetone (200—400 c.c.) and concentrated aqueous sodium hydroxide (about 70 c.c.) were mixed at the ordinary temperature and placed in an ice-chest for forty-eight hours. The acetone solution was then poured off from the solid mass, and neutralised by adding a few drops of acetic acid, after which the acetone was distilled off on the water-bath, and the residue fractionally distilled under the ordinary pressure. In this way the fraction 162—168° amounted to 18 per cent. of the acetone employed. The acetone regained was again added to the above-mentioned solid mass, and allowed to remain in ice-water for forty-eight hours. (A longer period did not improve the yield.) In this way 18 per cent. of diacetone alcohol could again be obtained. On reduction with 3 per cent. sodium amalgam, β-methylpentane-βδ-diol,

$OH{\cdot}CMe_2{\cdot}CH_2{\cdot}CHMe{\cdot}OH$,

was obtained:

D_4^{17} 0·9240 (hence $D_4^{16\cdot7}$ 0·9242).

n_α 1·42729, n_D 1·42976, n_β 1·43489, n_γ 1·43939 at 16·7°.

	M_α.	M_D.	$M_\beta - M_\alpha$.	$M_\gamma - M_\alpha$.
Found	32·83	32·99	0·51	0·81
Calc. for $C_6H_{14}O_2$	32·81	32·96	0·48	0·77
Δ	+0·02	+0·03	+0·03	+0·03

The glycol was converted into the dibromide by means of hydrobromic acid. On adding the dibromide to a mixture of zinc dust and alcohol, reaction instantly took place, and the resulting product was washed with water, dried, and distilled over sodium. About half the quantity boiled at 59—60°/768 mm. It decolorised potassium permanganate instantly:

$D_4^{15\cdot3}$ 0·6888 (hence $D_4^{14\cdot5}$ 0·6894).

n_α 1·38738, n_D 1·38995, n_β 1·39505, n_γ 1·39975 at 14·5°.

	M_α.	M_D.	$M_\beta - M_\alpha$.	$M_\gamma - M_\alpha$.
Found	28·75	28·91	0·50	0·81
Calc. for C_6H_{12}	27·58	27·71	0·42	0·68
Δ	+1·17	+1·20	+0·08	+0·13

The numbers given by Zelinsky and Zelikoff are D_4^{19} 0·6832 and n_D^{19} 1·3860, and hence the substances are to be regarded as identical.

Tanacetone.

This substance was supplied by Schimmel & Co., nearly all distilled at 90—92°/15 mm. It had, in a 1-dcm. tube, $[\alpha]_D$ + 68·42°. As it still decolorised potassium permanganate, the semicarbazone was prepared, and after recrystallisation from methyl alcohol it melted at 173—174°. The tanacetone was obtained from the pure semicarbazone by means of oxalic acid, and the colourless product boiled at 201—202°/760 mm. In this condition it was stable towards permanganate for one to two minutes. The following data were obtained:

$D_4^{15\cdot1}$ 0·9193 (hence $D_4^{13\cdot6}$ 0·9205).

n_α 1·45133, n_D 1·45401, n_β 1·45967, n_γ 1·46457 at 13·6.°

	M_α.	M_D.	$M_\beta - M_\alpha$.	$M_\gamma - M_\alpha$.
Found	44·52	44·75	0·71	1·12
Calc. for $C_{10}H_{16}O$	43·80	43·99	0·67	1·10
Δ	+0·72	+0·76	+0·04	+0·02

Tanacetyl Alcohol.

This was obtained by the reduction of tanacetone with sodium and alcohol. It was quite stable towards permanganate, and boiled at 209·8—210·1°/757 mm. The following data were obtained:

$D_4^{19\cdot1}$ 0·9202 (hence $D_4^{17\cdot2}$ 0·9217).

n_α 1·46115, n_D 1·46379, n_β 1·46961, n_γ 1·47471 at 17·2°.

	M_α.	M_D.	$M_\beta - M_\alpha$.	$M_\gamma - M_\alpha$.
Found	45·89	46·12	0·72	1·14
Calc. for $C_{10}H_{18}O$	45·31	45·51	0·67	1·12
Δ	+0·58	+0·62	+0·05	+0·02

The phenylurethane was prepared, but did not crystallise, although many solvents were tried, and the viscid, oily product was allowed to remain in a vacuum for about a month. On distillation the product began to pass over at 160°/13 mm., but decomposed.

Methyl α-Thujaketonate.

The acid was obtained by oxidising tanacetone with potassium permanganate in the cold. The yield was satisfactory, and only a very small quantity of the isomeric β-acid was obtained. The ester of the α-acid was prepared from the silver salt and methyl iodide. It is not attacked by permanganate. The following data were obtained:

$D_4^{18\cdot1}$ 1·0126 (hence D_4^{17} 1·0133).

n_α 1·45380, n_D 1·45642, n_β 1·46267, n_γ 1·46796 at 17°.

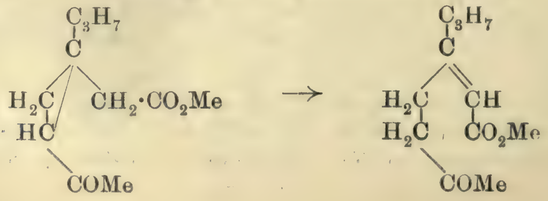
	M_α	M_D.	$M_\beta - M_\alpha$.	$M_\gamma - M_\alpha$.
Found	52·92	53·19	0·89	1·42
Calc. for $C_{11}H_{18}O_3$	52·22	52·46	0·81	1·32
Δ	+0·70	+0·73	+0·08	+0·10

By distilling in a vacuum a product was obtained which instantly decolorised potassium permanganate, and gave the following constants:

$D_4^{17\cdot7}$ 0·9940 (hence $D_4^{16\cdot85}$ 0·9947).

n_α 1·46422, n_D 1·46758, n_β 1·47571, n_γ 1·48292 at 16·85°.

As by distillation of the α-acid the β-acid is formed, it is assumed that the following rearrangement takes place:



The optical data give:

	M_α.	M_D.	$M_\beta - M_\alpha$.	$M_\gamma - M_\alpha$.
Found	54·98	55·32	1·16	1·89
Calc. for $C_{11}H_{18}O_3\vert^{=}$...	53·91	54·19	0·95	1·52
Δ	+1·07	+1·13	+0·21	+0·37
EΣ	+0·54	+0·57	+22%	+24%

These increments are in accordance with others found for similarly conjugated double linkings (Auwers and Eisenlohr, *loc. cit.*)

Dimethyl α-Tanacetonedicarboxylate.

The acid was obtained by oxidation of the α-ketonic acid with sodium hypobromite. The dimethyl ester obtained in two different ways boiled at 241—242° under the ordinary pressure and at 126—127°/12 mm. The following data were obtained:

$D_4^{18\cdot9}$ 1·0535 (hence $D_4^{16\cdot5}$ 1·0554).
n_α 1·44964, n_D 1·45222, n_β 1·45809, n_γ 1·46321 at 16·5°.

	M_α.	M_D.	$M_\beta - M_\alpha$.	$M_\gamma - M_\alpha$.
Found	54·48	54·75	0·88	1·42
Calc. for $C_{11}H_{18}O_4$ ...	53·86	54·10	0·82	1·34
Δ	+0·62	+0·65	+0·06	+0·08

α-Thujene.

B. p. 151—152°/755 mm. $D_4^{17\cdot4}$ 0·8294 (hence $D_4^{15\cdot65}$ 0·8308).
n_α 1·44901, n_D 1·45182, n_β 1·45864, n_γ 1·46434 at 15·65°.

	M_α.	M_D.	$M_\beta - M_\alpha$.	$M_\gamma - M_\alpha$.
Found	43·94	44·18	0·81	1·29
Calc. for $C_{10}H_{16}\vert^{=}$.....	43·29	43·51	0·75	1·22
Δ	+0·65	+0·67	+0·06	+0·07

Thujane.

B. p. 156·2—156·8°/756 mm. $D_4^{19\cdot5}$ 0·8142 (hence $D_4^{20\cdot2}$ 0·8136).
n_α 1·43708, n_D 1·43939, n_β 1·44495, n_γ 1·44983 at 20·2°.

	M_α.	M_D.	$M_\beta - M_\alpha$.	$M_\gamma - M_\alpha$.
Found	44·48	44·68	0·69	1·12
Calc. for $C_{10}H_{18}$	43·79	43·98	0·66	1·08
Δ	+0·69	+0·70	+0·03	+0·04

Cyclene.

The cyclene, which was mixed with camphene, was purified by means of heating it with powdered potassium permanganate and glacial acetic acid to 70—80° for ten hours. It boiled at 153°/761 mm., and had the following constants:

D_4^{66} 0·8440 (hence $D_4^{66\cdot9}$ 0·8433).
n_α 1·43816, n_D 1·44055, n_β 1·44644, n_γ 1·44975 at 66·9°.

	M_α.	M_D.	$M_\beta - M_\alpha$.	$M_\gamma - M_\alpha$
Found	42·38	42·58	0·69	0·97
Calc. for $C_{10}H_{16}$	41·61	41·78	0·62	1·02
Δ	+0·77	+0·80	+0·07	−0·05

The reading of the γ-line was uncertain.

β-Pinolene or cyclo*Fenchene.*

The terpene fraction 141—144° was freed from admixed unsaturated α-pinolene in the same way as described above. It boiled at 143—143·5°/748 mm., and had the following constants:

$D_4^{16\cdot2}$ 0·8624.
n_α 1·45104, n_D 1·45370, n_β 1·45968, n_γ 1·46449 at 16·2°.

	M_α.	M_D.	$M_\beta - M_\alpha$.	$M_\gamma - M_\alpha$.
Found	42·50	42·71	0·69	1·09
Calc. for $C_{10}H_{16}$	41·61	41·78	0·62	1·02
Δ	+0·89	+0·95	+0·07	+0·07

After being shaken with potassium permanganate solution for four days the same constants were obtained.

cyclo*Propanecarboxylic Acid.*

The acid was prepared by condensing ethylene bromide with malonic ester and also with cyanoacetic ester (Carpenter and Perkin, Trans., 1899, **75**, 921) and subsequent saponification and heating.

The distillate boiling at 183·2—184°/760 mm. was then further purified by cooling in a freezing mixture, and the well-defined crystals were dried on a cooled porous plate. They melted at 9—10°. The following data were obtained:

$D_4^{19\cdot7}$ 1·0897 (hence $D_4^{20\cdot9}$ 1·0887).
n_α 1·43446, n_D 1·43698, n_β 1·44331, n_γ 1·44839 at 20·9°.

	M_α.	M_D.	$M_\beta - M_\alpha$.	$M_\gamma - M_\alpha$.
Found	20·59	20·69	0·35	0·57
Calc. for $C_4H_{16}O_2$	19·92	20·01	0·31	0·50
Δ	+0·67	+0·68	+0·04	+0·07

Methyl cyclo*Propanecarboxylate.*

The ester was obtained by the action of methyl iodide on the silver salt of the acid. (Found, C = 59·93; H = 8·11. Calc., C = 60·0;

H = 8·06 per cent.) It boiled at 119°/764 mm., and gave the following data:

$D_4^{20\cdot1}$ 0·9848 (hence $D_4^{19\cdot1}$ 0·9856).
n_α 1·41175, n_D 1·41439, n_β 1·41958, n_γ 1·42444 at 19·1°.

	M_α.	M_D.	$M_\beta - M_\alpha$.	$M_\gamma - M_\alpha$.
Found	25·26	25·40	0·42	0·68
Calc. for $C_5H_8O_2$	24·63	24·74	0·38	0·61
Δ	+0·63	+0·66	+0·04	+0·07

Diethyl cyclo*Propane*-1 : 1-*dicarboxylate*.

The ester was obtained from the pure acid (m. p. 140°) by boiling with a 3 per cent. solution of hydrogen chloride in ethyl alcohol. It boiled at 214—215°, and gave the following data:

$D_4^{19\cdot1}$ 1·0624 (hence D_4^{18} 1·0633).
n_α 1·43183, n_D 1·43447, n_β 1·43994, n_γ 1·44476 at 18°.

	M_α.	M_D.	$M - M_\alpha$.	$M_\gamma - M_\alpha$.
Found	45·38	45·62	0·72	1·18
Calc. for $C_9H_{14}O_4$......	44·67	44·88	0·68	1·11
Δ	+0·71	+0·74	+0·04	+0·07

The ester was not acted on by permanganate.

Dimethyl cyclo*Propane*-1 : 2-*dicarboxylate*.

The acid was obtained (with a slight modification) as described by Perkin (*Ber.*, 1886, **19**, 1053) and Dressel (*Annalen*, 1889, **256**, 193). The dimethyl ester boiled at 219—220°/760 mm. (Found, C = 53·06; H = 6·51. Calc., C = 53·16; H = 6·33 per cent.) The following data were obtained:

$D_4^{15\cdot9}$ 1·1584 (hence $D_4^{14\cdot3}$ 1·1597).
n_α 1·44442, n_D 1·44717, n_β 1·45297, n_γ 1·45812 at 14·3°.

	M_α.	M_D.	$M_\beta - M_\alpha$.	$M_\gamma - M_\alpha$.
Found	36·24	36·44	0·61	0·97
Calc. for $C_7H_{10}O_4$	35·47	35·63	0·54	0·88
Δ	+0·77	+0·81	+0·07	+0·09

cyclo*Butanecarboxylic Acid*.

B. p. 195—195·6°/759 mm. $D_4^{18\cdot1}$ 1·0577 (hence D_4^{19} 1 0570).
n_α 1·44071, n_D 1 44336, n_β 1·44896, n_γ 1·45385 at 19°.

	M_α.	M_D.	$M_\beta - M_\alpha$.	$M_\gamma - M_\alpha$.
Found	24·99	25·12	0·39	0·65
Calc. for $C_5H_8O_2$	24·52	24·63	0·37	0·61
Δ	+0·47	+0·49	+0·02	+0·04

When cooled in solid carbon dioxide the acid crystallised in long needles melting at −6°.

Ethyl cyclo*Butanecarboxylate.*

The ester was obtained by boiling the acid with 3 per cent. ethyl-alcoholic hydrogen chloride. It boiled at 151°/750 mm., and was not acted on by permanganate. The following data were obtained:

$D_4^{19\cdot85}$ 0·9525 (hence $D_4^{18\cdot5}$ 0·9536).

n_α 1·42339, n_D 1·42587, n_β 1·43094, n_γ 1·43575 at 18·5°.

	M_α.	M_D.	$M_\beta - M_\alpha$.	$M_\gamma - M_\alpha$.
Found	34·23	34·41	0·54	0·87
Calc. for $C_7H_{12}O_2$	33·83	33·98	0·52	0·84
Δ	+0·40	+0·43	+0·02	+0·03

Nopinone.

B. p. 118·2°/43 mm. $D_4^{15\cdot65}$ 0·9827 (hence $D_4^{15\cdot55}$ 0·9820).

ν_α 1·47666, n_D 1·47981, n_β 1·48592, n_γ 1·49142 at 15·55°.

	M_α.	M_D.	$M_\beta - M_\alpha$.	$M_\gamma - M_\alpha$.
Found	39·71	39·94	0·66	1·05
Calc. for $C_9H_{14}O$	39·20	39·37	0·60	0·99
Δ	+0·51	+0·57	+0·06	+0·06

Dimethyl cyclo*Butane*-1:2-*dicarboxylate.*

The acid was prepared by the method described by Perkin (Trans., 1894, **65**, 572). The ester boiled at 114—114·5°/20 mm., and gave the following data:

$D_4^{17\cdot3}$ 1·1191 (hence $D_4^{17\cdot8}$ 1·1187).

n_α 1·44051, n_D 1·44300, n_β 1·44835, n_γ 1·45341 at 17·8°.

	M_α.	M_D.	$M_\beta - M_\alpha$.	$M_\gamma - M_\alpha$.
Found	40·59	40·79	0·62	1·02
Calc. for $C_8H_{12}O_4$	40·07	40·25	0·61	0·99
Δ	+0·52	+0·54	+0·01	+0·03

Methyl Pinonate.

The ester was not acted on by permanganate. It boiled at 127·6—128°/11 mm. and 254—255°/755 mm. The following data were obtained:

$D_4^{15\cdot2}$ 1·0187 (hence $D_4^{16\cdot6}$ 1·0176).

n_α 1·45300, n_D 1·45582, n_β 1·46158, n_γ 1·46679 at 16·6°.

	M_α.	M_D.	$M_\beta - M_\alpha$.	$M_\gamma - M_\alpha$.
Found	52·62	52·90	0·86	1·37
Calc. for $C_{11}H_{18}O_3$ ...	52·22	52·46	0·81	1·32
Δ	+0·40	+0·44	+0·05	+0·05

Dimethyl Norpinate.

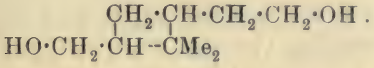
*cis*Norpinic acid was obtained from pinonic acid according to the method described by Baeyer (*Ber.*, 1896, **29**, 1908). After several recrystallisations from ether it melted at 173—174°. The dimethyl ester boiled at 113—113·8°/11 mm. and 228—229°/756 mm. The following data were obtained:

$D_{4}^{14\cdot3}$ 1·0700 (hence D_{4}^{17} 1·0678).

n_{α} 1·44341, n_{D} 1·44591, n_{β} 1·45142, n_{γ} 1·45643 at 17°.

	M_{α}.	M_{D}.	$M_{\beta}-M_{\alpha}$.	$M_{\gamma}-M_{\alpha}$.
Found	49·72	49·96	0·78	1·26
Calc. for $C_{10}H_{16}O_4$ ...	49·27	49·49	0·75	1·22
Δ	+0·45	+0·47	+0·03	+0·04

Glycol from Ethyl Pinate,



$$\begin{array}{l} \quad\;\; CH_2\cdot CH\cdot CH_2\cdot CH_2\cdot OH\,. \\ HO\cdot CH_2\cdot CH-CMe_2 \end{array}$$

This glycol was obtained by reducing ethyl pinate with sodium and alcohol:

0·1308 gave 0·3293 CO_2 and 0·1365 H_2O. C = 68·67; H = 11·68.

$C_9H_{18}O_2$ requires C = 68·31; H = 11·45 per cent.

It is very viscid, and has a slightly unpleasant, aromatic odour. It boiled at 166—167°/17 mm., and gave the following constants:

$D_{4}^{19\cdot8}$ 0·9947 (hence $D_{4}^{19\cdot7}$ 0·9948).

n_{α} 1·47438, n_{D} 1·47710, n_{β} 1·48296, n_{γ} 1·48810 at 19·7°.

	M_{α}.	M_{D}.	$M_{\beta}-M_{\alpha}$.	$M_{\gamma}-M_{\alpha}$.
Found	44·71	44·92	0·68	1·09
Calc. for $C_9H_{18}O_2$ ...	44·43	44·61	0·65	1·06
Δ	+0·28	+0·31	+0·03	+0·03

Dimethyl cyclo*Pentane*-1 : 2-*dicarboxylate.*

The pure *trans*-acid melted at 163°. The dimethyl ester boiled at 118·5—119°/17 mm.:

$D_{4}^{19\cdot1}$ 1·1130 (hence $D_{4}^{17\cdot8}$ 1·1140).

n_{α} 1·44683, n_{D} 1·44900, n_{β} 1·45472, n_{γ} 1·45938 at 17·8°.

	M_{α}.	M_{D}.	$M_{\beta}-M_{\alpha}$.	$M_{\gamma}-M_{\alpha}$.
Found	44·62	44·81	0·68	1·08
Calc. for $C_9H_{14}O_4$	44·66	44·87	0·69	1·10
Δ	−0·04	−0·06	−0·01	−0·02

*Vinyl*cyclo*propane* (?).

This hydrocarbon was prepared according to Gustavson's method (*J. pr. Chem.*, 1896, [ii], **54**, 99) from pentaerythritol tetrabromohydrin. It was acted on by permanganate, and boiled at 42—42·8°/755 mm., and gave the following data:

D_4^{16} 0·7375 (hence $D_4^{16·7}$ 0·7370).

n_α 1·41615, n_D 1·41966, n_β 1·42635, n_γ 1·43241 at 16·7°.

	M_α.	M_D.	$M_\beta - M_\alpha$.	$M_\gamma - M_\alpha$.
Found	23·20	23·37	0·49	0·79
Calc. for C_5H_8	20·80	20·89	0·31	0·51
Δ	+2·40	+2·48	+0·18	+0·28
Calc. for $C_5H_8\|^{=}$	22·49	22·62	0·45	0·71
Δ	+0·71	+0·75	+0·04	+0·08

Dimethyl spiro*Heptanedicarboxylate.*

The acid was prepared as described by Fecht (*loc. cit.*). The tetracarboxylic acid first formed crystallised from light petroleum and ether in long needles, melting and decomposing at 211°:

0·1206 required for neutralisation 16·2 c.c. $N/10$-$Ba(OH)_2$; $C_{11}H_{12}O_8$ requires 17·7 c.c.

This acid forms a sparingly soluble *sodium hydrogen* salt, which crystallises well from water.

By heating in an oil-bath to 200—210° the dicarboxylic acid, $C_9H_{12}O_4$, was obtained, and was purified by recrystallisation from formic acid and from ethyl acetate, when it melted at 209°. (Found, C = 58·63; H = 6·56. Calc., C = 58·66; H = 6·57 per cent.):

0·1073 required for neutralisation 11·57 c.c. $N/10$-$Ba(OH)_2$; $C_9H_{12}O_4$ requires 11·65 c.c.

From the pure acid the *dimethyl* ester was obtained by heating it for three hours with 2 per cent. methyl-alcoholic hydrogen chloride. The ester is stable towards permanganate, and boils at 149°/18 mm.:

0·1020 gave 0·2327 CO_2 and 0·0710 H_2O. C = 62·23; H = 7·79.
$C_{11}H_{16}O_4$ requires C = 62·23; H = 7·59 per cent.

$D_4^{20·1}$ 1·0982 (hence $D_4^{19·1}$ 1·0990).

n_α 1·45935, n_D 1·46200, n_β 1·46850, n_γ 1·47291 at 19·1°.

	M_α.	M_D.	$M_\beta - M_\alpha$.	$M_\gamma - M_\alpha$.
Found	52·80	53·06	0·90	1·33
Calc. for $C_{11}H_{16}O_4$ ...	51·67	51·91	0·78	1·27
Δ	+1·13	+1·15	+0·12	+0·06

The acid melting at 209° was obtained by the hydrolysis of the ester.

THE UNIVERSITY,
MANCHESTER.

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[illegible]

MOISSAN MEMORIAL LECTURE.

DELIVERED ON FEBRUARY 29TH, 1912.

By SIR WILLIAM RAMSAY, K.C.B., F.R.S.

FRANCE has always held one of the highest places among the nations in the brilliance and originality of her sons. In the domain of chemistry, especially, many names of illustrious Frenchmen suggest themselves; Lavoisier, Guyton de Morveau, Berthollet, Gay-Lussac, Dumas, and Berthelot stand out among a crowd of others hardly less distinguished. We have recently heard from the eloquent lips of our late President, Professor Dixon, a charming account of the life and work of the last named of these eminent men; it is my duty to-night to ask you to listen to a brief discourse on a contemporary of Berthelot's, who, though cut off by fate at a comparatively early age, stood only second to him among the representatives of chemistry in France in his time.

Henri Moissan was born in Paris on September 28th, 1852. His father was a native of Toulouse; his mother, whose maiden name was Mitelle, was of an Orleans family. Moissan's features and his bright, vivacious manner betrayed his southern origin; he was of the best French type.*

His education, after school life, began in the Collège de Meaux, and in his twentieth year he entered the laboratory of Frémy at the Musée d'Histoire Naturelle, attending at the same time the lectures of Henri Sainte-Claire Deville and Debray. He made good progress, and after spending a year at elementary work he removed to the neighbouring laboratory of Decaisne and Dehérain, in the École Pratique des Hautes Études, with whom he worked on practical problems bearing on vegetable life. Whilst there, he passed the examinations required for graduation, taking the preliminary degree of Bachelier in 1874; of Licentié in 1877; in 1879 he became "Pharmacien de première Classe"; and in 1880 he qualified as "Docteur ès Sciences physiques."

After working with Dehérain for little more than a year, he left the Museum to direct a small laboratory of his own; and he then abandoned the study of vegetable chemistry for that of inorganic chemistry, a branch to which he remained faithful during the rest of his life, and in which he achieved the highest distinction. This private laboratory was given up somewhat later; and he then found quarters with MM. Debray and Troost, in the laboratories of the Sorbonne, of which in after time he was to become Director.

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* Madame Moissan has had the kindness to place at my disposal the photographs and specimens exhibited during the lecture.

In 1879 he was appointed "Répétiteur de Physique" at the Agronomic Institute, and after spending a year in that position he was promoted to the post of "Maître de Conférences" and "Chef des Travaux Pratiques," or lecture assistant and senior demonstrator at the Ecole Supérieure de Pharmacie, a position which he held until 1883. A year before this change, he had been appointed, after a competitive examination, "Agrégé des Sciences physiques-chimiques," and his standing among his fellows at that date was such that on the death of Professor Bouis in 1886 he was elected to the Professorship of Toxicology in the School of Pharmacy; he retained that Chair until 1899, when his turn came in rotation to occupy the Chair of "Mineral" or Inorganic Chemistry; he then for the first time delivered a course of lectures on that branch of chemistry.

In 1900 he was appointed Assessor to the Director of that School, and in the same year, on the retirement of Professor Troost, the Professor of Inorganic Chemistry in the Faculté des Sciences in the University of Paris, Moissan was unanimously chosen as his successor, for his name had become very widely known owing to his remarkable discoveries. At the same time, he retained the title of Honorary Professor at his old school, the École de Pharmacie.

Moissan's first research was conducted in conjunction with Dehérain; it had reference to the interchange of oxygen and carbon dioxide in the leaves of plants which had been exposed to the subdued light of a darkened room.

His first work in the domain of inorganic chemistry dealt with the oxides of the iron group of metals, and especially with the compounds of chromium. His thesis for the doctorate contained an account of a portion of this research. In it he described the existence of two allotropic modifications of chromium sesquioxide; one obtained by igniting ammonium chromate, as well as by other methods, insoluble in acids, unattacked by hydrogen sulphide and by oxygen; the other, produced by careful drying of the hydrated oxide at 440°, which, when heated to 140° in a current of hydrogen sulphide, gave a black sulphide, Cr_2S_3, reducible to chromous sulphide, CrS, by further heating in a current of hydrogen. Oxygen converted this variety of sesquioxide into the analogue of manganese dioxide, CrO_2, a dark grey powder.

This train of thought led Moissan to investigate the products of reduction of the oxides of the iron group. The so-called "pyrophoric iron," obtained by heating ferrous oxalate, was shown to consist of ferrous oxide, FeO; the same substance is produced by reducing the oxide, Fe_2O_3, in a current of a mixture of carbon dioxide and hydrogen. The action of hydrogen at 330—440° reduces Fe_2O_3 to Fe_3O_4, and the magnetic oxide is also formed by heating the sesquioxide in a current of carbon monoxide at the temperature of melting zinc. It is only at 500—600° that ferrous oxide is produced; it is pyrophoric at the ordinary temperature. But pyrophoric iron itself can be obtained by heating the sesquioxide for a long time in a current of perfectly dry hydrogen to 440°, or by distilling away the mercury from an amalgam of iron. The amalgam, indeed, prepared by electrolysing a solution of ferrous chloride with mercury as the cathode, turns very hot on exposure to air.

An allotropic variety of the magnetic oxide, Fe_3O_4, was produced by heating the monoxide, or metallic iron reduced by hydrogen, to redness in a current of moist hydrogen. It formed a black magnetic powder, incandescing and changing to Fe_2O_3 when heated in air. At 1500° Fe_2O_3 gave off oxygen, and was converted into a very resisting modification of the magnetic oxide.

Somewhat similar researches were carried out on the oxides of manganese, nickel, and cobalt, and pyrophoric varieties of the metals were prepared.

Having obtained metallic chromium from its amalgam, Moissan next investigated the little-known chromous salts, preparing pure chromous chloride, $CrCl_2$; also the blue sulphate, $CrSO_4,7H_2O$, which is isomorphous with copperas; also chromous bromide, chromous acetate, and chromous oxalate. The acetate or chloride, on treatment with a solution of potassium cyanide, gave the interesting compound, $K_4CrC_6N_6$, analogous to yellow prussiate of potash, oxidisable to the red $K_3CrC_6N_6$. A final paper on the blue compound of CrO_3 with peroxide of hydrogen, in which it was shown that the ratio between the two is $CrO_3 : H_2O_2$, ends the series.

In 1884 Moissan turned his attention to the investigation of compounds of fluorine. He prepared phosphorus fluoride first, by heating copper phosphide with lead fluoride. It is a gas, exploding when sparked with oxygen, and yielding the oxyfluoride, POF_3. He next prepared fluoride of arsenic, by distilling a mixture of arsenious oxide, sulphuric acid, and calcium fluoride. He electrolysed this liquid, and produced from it elementary arsenic, and a gas which attacked the platinum electrode. On submitting phosphorous fluoride to a rain of sparks, phosphorus was deposited; the product, however, was not fluorine, but phosphoric fluoride, PF_5, the liberated fluorine combining with the phosphorous fluoride. These researches occupied him until 1888. In that year he investigated some organic fluorides, obtaining ethyl fluoride, C_2H_5F, by the interaction of ethyl iodide and silver fluoride, and the corresponding methyl and *iso*butyl fluorides. In the following year he made the capital discovery that whilst the compound KF,2HF melts at 65°, KF,3HF remains liquid at $-23°$, and conducts electricity electrolytically; and this long series of researches culminated in the discovery of elementary fluorine.

During this work he accumulated useful information, which enabled him to adapt his apparatus to the end he had in view. One method which he attempted for the isolation of fluorine was to pass phosphorous and phosphoric fluorides over red-hot platinum sponge. A gas was evolved which liberated iodine from a solution of potassium iodide; but this gas came off very slowly, and was largely absorbed by the platinum tube in which the experiment was made. He next tried the electrolysis of arsenious fluoride; but he found that that liquid is a very poor conductor, and he attempted to increase its conductivity by the addition of anhydrous hydrogen fluoride; better results, however, were obtained on addition of anhydrous potassium fluoride to the mixture of arsenious fluoride and hydrogen fluoride; and from this it was but a step to omit the arsenious fluoride and to electrolyse the mixture of acid and potassium salt.

His first apparatus was made of platinum; the electrodes were rods of platinum-iridium alloy, thickened at the ends so as to last longer, for the negative electrode was always rapidly corroded. Paraffined corks closed the ends of his first platinum U-tube. The cork closing the limb into which the negative electrode passed was corroded and charred; hence in his next experiment, corks were replaced by fluor-spar stoppers, cemented into hollow platinum cases, on which a screw was turned, so that the stoppers could be screwed tight into the open ends of the U-tube. This experiment was successful in yielding fluorine; whilst hydrogen came off at the negative electrode, and passed out through a side-branch of platinum tube, fluorine was evolved at the positive pole; it passed out through a similar platinum tube, and was made to play on various materials exposed to its action in a platinum capsule. It was subsequently discovered that as copper exposed to fluorine immediately becomes covered with a deposit of the fluoride, which protects it from further action, copper could be substituted for platinum in the structure of the U-tube, and an important economy could thus be effected.

It was found that sulphur, selenium, and tellurium inflamed, giving white deposits; the first combines, as Moissan subsequently found, to form a gas, SF_6, sulphur hexafluoride. From phosphorus, PF_3 and PF_5 were obtained; iodine caught fire and burned; Moissan subsequently found that IF_5 was the product; bromine lost its colour, and later, Moissan and his pupils proved this to be due to the formation of BrF_3; on pure carbon at the ordinary temperature fluorine had no action; but both boron and silicon caught fire and burned, giving SiF_4 and BF_3.

By blocking the exit of either of the tubes conveying away the hydrogen or the fluorine, one or other gas could be caused to pass round the bend and mix; when a bubble passed round, a detonation occurred, showing that hydrogen and fluorine combine even in the dark at the low temperature of $-35°$, for the apparatus had to be maintained at this low temperature to prevent the admixture of gaseous hydrogen fluoride with the fluorine. The low temperature was conveniently attained by surrounding the U-tube with liquid methyl chloride.

Most metals were instantly attacked, some with inflammation; even platinum and gold could not resist its action; but they had to be raised to 400° before attack took place. Salts such as potassium iodide, mercuric iodide, and lead iodide were completely decomposed, giving fluorides both of the metal and of the iodine. Chlorine was liberated from potassium chlorate, along with oxygen, on which fluorine had no action; chlorine was also evolved from carbon tetrachloride, the tetrafluoride being formed; and water was instantly decomposed, its oxygen being liberated partly as ozone.

Although all these properties of this gas could be most easily explained on the assumption that it consisted of fluorine, still they might conceivably appertain to a mixture of ozone and hydrofluoric acid, or to a perfluoride of hydrogen, HF_n. The former supposition was disproved by trying the action of such a mixture; but none of the properties of the gas was manifested. The second hypothesis was also disproved by leading the fluorine over iron, and proving that no hydrogen passed on.

Subsequent research showed that the formation of fluorine was not so simple as had at first been supposed. Investigation of a muddy deposit, which was always found at the bend of the U-tube on dismantling it, showed that that substance consisted mainly of potassium platinifluoride, K_2PtF_6, and that in all probability it was the substance undergoing electrolysis, the equivalent of the potassium being liberated at the cathode as hydrogen, and fluorine at the anode, the group PtF_4 again combining with potassium fluoride. The operation did not proceed with regularity until a considerable quantity of platinum had dissolved from the anode.

The density of the gas was found to be 18·3, on the hydrogen standard. This figure, which is too low, was almost certainly due to the presence of oxygen, produced by the electrolysis of water still dissolved in the electrolytic mixture. Moissan for long supposed that, on passing the current, the water accidentally present first underwent electrolysis before the fluorine appeared; but it was subsequently found that water still remained to be electrolysed, even after much fluorine had been separated. Later experiments, in which the gases other than fluorine were estimated in the gaseous mixture, weighed, and allowance was made for their presence, proved that the true density of fluorine is 19, a figure identical with the atomic weight. The supposition that fluorine consisted partly of monatomic molecules mixed with an excess of diatomic molecules had therefore to be abandoned. The activity of fluorine was not to be explained by its monatomicity.

The reason why fluorine cannot be produced by heating tetrafluoride of platinum, PtF_4, was found as soon as that substance had been prepared by the action of fluorine on platinum; it is because that compound decomposes water, and therefore cannot be prepared in the wet way.

Moissan also attempted to induce combination between argon and fluorine, and helium and fluorine, but without success, even when the mixture was submitted to the discharge of powerful sparks.

The preparation of two gaseous fluorides of carbon led Moissan to attempt to remove the fluorine, in the hope that the carbon would be liberated in the form of diamond. But this hope was disappointed; the product was always lamp-black. These experiments, however, led to the discovery of the method of preparing the diamond artificially; it had been found that a meteorite from Cañon Diablo, consisting, as meteorites usually do, mainly of metallic iron, had imbedded in it small crystals of diamond; and Moissan's genius led him to devise the cause of their formation; his theory was that the carbon had originally been dissolved in the iron when it was in a molten state; that the surface of the iron had suddenly cooled, and that the iron in the interior, on solidifying, was subjected to great pressure, for solid iron containing carbon in solution occupies a larger volume than molten iron. These considerations directed his experiments, which were crowned with success.

His first experiments, however, in which the iron was saturated with carbon at about 1000°, were not successful; he accordingly argued that at higher temperatures the solubility of carbon in iron should increase, as is the general rule; and he devised the electric furnace to attain much higher temperatures. His three great investigations are thus seen to hang together; one suggested the other, and Moissan's skill and patience brought all to a successful conclusion. The spirit in which he carried out his work is well expressed in his own words, which occur in the preface to his book on the "Electric Furnace": "But what I cannot convey in the following pages is the keen pleasure which I have experienced in the pursuit of these discoveries. To plough a new furrow; to have full scope to follow my own inclination; to see on all sides new subjects of study bursting upon me; that awakens a true joy which only those can experience who have themselves tasted the delights of research."

Moissan's electric furnace, designed not for technical, but purely for experimental work, was of the simplest construction. It consisted of a rectangular block of lime, made of the excellent Paris limestone, in the centre of which a hole had been scooped. This block was covered with a rectangular lid; two grooves of circular section admitted the carbon poles which served as electrodes, and an arc was made between the poles. Later, an electromagnet was used to deflect the arc downwards, so that it might play more directly on the object to be heated. A current of 100 to 125 amperes at 50 or 60 volts was employed in his earlier researches.

The volatilisation of the material of the furnace, lime, was the first fact to be chronicled. Indeed, two torrents of what appeared to be flame poured out through the holes admitting the electrodes. These apparent flames were, however, only white-hot lime dust, condensed from the lime-vapour which filled the furnace. Subsequently, to save cost, the body of the furnace was constructed of limestone. The crucible to be heated stood on magnesia, to avoid the rapid formation of calcium carbide; and for some purposes, crucibles were constructed of a grid of alternate slices of carbon and magnesia. By heating an inclined carbon tube in the arc, and feeding in at one end a mixture of an oxide such as chromium oxide and carbon, the metal flowed out at the other end, and a continuous supply was thus obtainable.

The temperature of the electric furnace appeared to depend on the quantity and intensity of the current; but it is limited, no doubt, by the temperature of volatisation of carbon.

By help of this powerful engine of research, Moissan succeeded in causing many changes to occur, and in producing many compounds previously unknown. Some of these compounds have had important commercial applications; others are of great interest, owing to the reactions which they undergo, and the light that they shed on the problems of chemical combination.

In his systematic search for a method of producing artificial diamonds, Moissan investigated numerous varieties of graphite; he subjected different kinds of carbon to the intense heat of the electric furnace, in order to study their behaviour, and, as before remarked, he studied the Cañon Diablo meteorite, in which small diamonds are embedded. These researches made him familiar with the behaviour of carbon in all possible circumstances, and enabled him to separate diamonds from other materials with which they might be mixed.

The first actual experiment of crystallising carbon under pressure from iron was made with 200 grams of Swedish iron, fused in the electric furnace for six minutes with sugar-charcoal in a carbon crucible. The crucible was then seized with tongs, and plunged into a vessel full of cold water. Moissan relates the anxiety with which this was first attempted; an explosion was feared; but, although the water boiled, no accident occurred then, or, indeed, during some hundreds of similar experiments. The iron was dissolved in dilute hydrochloric acid; the residue, chiefly consisting of carbon in various forms, was extracted with nitrohydrochloric acid, and alternately with boiling sulphuric and hydrofluoric acids. It was then, in order to remove graphite, boiled with nitric acid and potassium chlorate. The final residue was floated in bromoform, in which some transparent dust, of density 3 to 3·5, sank, whilst a black substance floated. The transparent particles scratched ruby, burned to carbon dioxide, and showed octahedral facets.

Among the other products of the electric furnace were: crystallised lime, strontia, baryta, and magnesia; metallic and reguline chromium, manganese, molybdenum, tungsten, uranium, vanadium, zirconium, and titanium; also distilled copper, silver, platinum, gold, tin, iron, and uranium; volatilised carbon and silicon, and many other similar products. The metals were obtained by heating the oxides mixed with powdered sugar-charcoal; and in most cases a carbide of the metal, or a solution of carbide in the metal, was obtained. The presence of carbon monoxide, due to the presence of the carbon electrodes, no doubt contributed to the formation of carbide. In order to obtain the pure metal, therefore, a second operation was necessary, as a rule; the metal was again heated in the furnace in a crucible lined with its own oxide; the combined carbon thus obtained oxygen, and was evolved as oxide, whilst the metal was left in the reguline state.

Moissan made an exhaustive study of the properties of the compact metals, and of their carbides. It would be impossible in a discourse like the present one to do justice to the enormous number of interesting observations which he made; indeed, he added a very large chapter to the book of chemistry. All that can be done is to pick out a few examples to illustrate the character of his work.

Let us first take chromium. This metal was prepared by allowing a mixture of the sesquioxide with carbon to run down a sloping tube of carbon, heated to whiteness in the electric furnace; metallic chromium ran out at the lower end, and Moissan says that it is easy to prepare as much as 20 kilograms of chromium at one operation. The amount of carbon in the product varied between 8·6 and 11·92 per cent. The carbides of this metal were then studied. On melting metallic chromium with a large excess of carbon in the furnace for ten or fifteen minutes, a brittle button was obtained, consisting of crystals of C_2Cr_3. It is unattacked by concentrated hydrochloric acid, by weak or strong nitric acid, or by *aqua regia*, but is acted on slowly by dilute hydrochloric acid. Nor is it attacked by fused potassium hydroxide, although potassium nitrate destroys it easily. Another carbide was produced during the preparation of metallic chromium, covering the surface of the metal with brilliant needles; its formula was CCr_4.

The carbide, produced as the raw material, was converted into the metal by the method already indicated, that is, by fusing it in a crucible lined with chromium oxide, and covering it with the same material. The button of metal thus obtained, however, was "burnt," that is, contained oxide in solution. To remove the oxide, it can be re-melted with lime; or, what is simpler, the original carbide can be deprived of carbon by fusion with lime, the lime forming calcium carbide, together with carbon monoxide. This action is, however, a reversible one; there is a double oxide of chromium and calcium formed, which forms fine crystals. This substance, fused with more carbide, yielded pure chromium. Chromium was found to be unalterable in air, but when heated to 2000° in oxygen it burned, emitting sparks even more brilliantly than iron does. Chromium filings heated with sulphur become incandescent, producing the sulphide. When heated with carbon, CCr_4 is produced. A silicide is produced when chromium and silicon are heated together in the electric furnace, which is very hard, scratching the ruby, and not attacked by acids, or by fused potash or nitre.

This method of refining chromium was applied to commercial "ferro-chrome," and was found to be successful in depriving it of carbon; and it was shown that, starting from chrome-iron ore, ferro-chrome of 60 per cent. chromium could be made by passing it, mixed with carbon, through the electrically heated tube; it contained 6 per cent. of carbon and 1 per cent. of silicon. Potassium or sodium chromate could be made from it by fusion with potassium or sodium nitrate, the iron remaining behind as insoluble oxide. In conclusion, Moissan found that copper, allied with half a per cent. of chromium, acquired twice the tensile strength of pure copper; it took a fine polish, and was less tarnished on exposure to air than copper.

In a similar manner he treats of manganese, molybdenum, tungsten, uranium, vanadium, zirconium, titanium, silicon (incidentally having discovered "carborundum"); he finds that aluminium is not easily reduced in the furnace, but yields a carbide. In this connexion he in some measure anticipates the "thermite" process, for he projects a mixture of aluminium filings with the oxide of the metal to be produced on to the surface of molten aluminium; in this way he prepared alloys of nickel, molybdenum, tungsten, uranium, and titanium with aluminium.

Moissan also prepared numerous carbides, and submitted them to an exhaustive study. Lithium carbide, prepared from lithium carbonate and carbon in the furnace, has the formula Li_2C_2, and on treatment with water yields pure acetylene.

In our *Proceedings* of the year 1893, Travers described the preparation for the first time of calcium carbide by heating together metallic sodium, calcium chloride, and carbon. A month before, Moissan had stated that the lime of his furnace reacted with the carbon of his electrodes, "forming a carbide of calcium, easy to collect." But it was not until March, 1894, that he described this compound, since become so important industrially. Travers used his carbide for the production of acetylene; but Wilson, who patented the same compound in 1893, in America, was ignorant that the gas evolved on treating it with water was acetylene; indeed, he does not appear to have treated it with water at all. Moissan made a most careful study of this important compound, and described its chemical properties in great detail. He also made the carbides of barium and strontium; and he described the action on them of chlorine, bromine, iodine, sulphur, selenium, and phosphorus; in each case both metal and carbon combine with the element used for the attack.

The action of water on the carbides of cerium, lanthanum, yttrium, and thorium produced in a similar manner is not so simple; acetylene, ethylene, methane, and liquid and solid hydrocarbons were formed from C_2Ce, C_2La, C_2Y, and C_2Th. Aluminium carbide, however, has the formula C_3Al_4, and yields pure methane. Manganese carbide, in its turn, belongs to a different type; its formula is CMn_3; and with water, hydrogen and methane in equal volumes are the products; and uranium carbide, C_3U_2, gives methane and a complex mixture of liquid hydrocarbons.

From these experiments Moissan was induced to propound a theory of the formation of petroleum; he does not consider it exclusive of the production of hydrocarbons by the natural distillation of coal and shale; but he thinks that in certain formations, where the existence of such deposits is improbable, the occurrence of petroleum may be explained by the attack of carbides of the metals by water.

Moissan also prepared many silicides and borides. Among these were silicides of iron, of chromium, and of carbon; although he had obtained crystals of "carborundum" in 1891, he did not at that time publish any account of it; and he concedes the merit of its discovery to Acheson. The borides of iron, nickel, cobalt, calcium, strontium, barium, carbon, and some others were also prepared and carefully studied. These researches took many years, and are a model for accurate experimentation and luminous exposition. They were described in two works, "Le Fluor," published in 1887, and "Le Four Électrique," published ten years later. Since that date Moissan's chief researches dealt with: The preparation of metallic calcium by heating calcium iodide with sodium; its success depends on the easy attack of sodium by alcohol, whilst calcium is hardly affected. The investigation of sodium ammoniums and methyl-ammoniums, obtained by the action of sodium on liquid ammonia and on methylamine; and similar substances obtained from lithium and calcium. The preparation in the pure state of the hydrides of calcium, sodium, and potassium; he showed that these bodies are non-conductors of electricity, and that the hydrogen which they contain must be supposed to exist in combination as a non-metal, in contrast to its condition in palladium hydrogen alloy. In later papers on these compounds, he described a most ingenious formation of sodium formate by the action of carbon dioxide on sodium hydride, and of sodium hyposulphite, $Na_2S_2O_4$, by treating the hydride with sulphur dioxide.

Moissan did not, however, desert his old favourites, fluorine and the products of the electric furnace; for in later years he prepared thionyl fluoride, SOF_2, and sulphuryl fluoride, SO_2F_2, both gases; and he re-determined the density of fluorine in a dry glass vessel. The electric furnace yielded him metallic niobium and tantalum, many metals of the rare earths, and borides of silicon. A silicide of lithium, Li_6Si_2, was prepared; and a new hydride of silicon, Si_2H_6, the analogue of ethane. He also studied the acetylides of metals of the alkalis. His last research, of which an account appeared in the *Compt. rendus* for 1906, p. 675, dealt with the distillation of titanium in the electric furnace. In all, he published more than three hundred memoirs and notices.

This incomplete account of Moissan's work shows how productive his laboratory was; he was full of new ideas, most of them offshoots of his original great discoveries; much of his work was carried out in conjunction with students, of whom an increasing number came from abroad, for his reputation both as a skilled chemist and as an attractive personality had become world-wide. His work lay almost entirely in the field of inorganic chemistry, and it contributed to turn the tide which had set so long in favour of organic research.

He published, along with many other collaborators, a treatise on inorganic chemistry—"Traité de Chimie Minerale"—in five large volumes, which has a large circulation in France, and in point of detail is a very complete account of inorganic compounds.

Moissan was the recipient of numerous honours, not only in his own country, but also abroad. In 1888, after his isolation of fluorine, he was elected a member of the Académie de Medecine; in 1891, of the Académie des Sciences; in 1895, Membre of the Conseil d'Hygiène de la Seine; and in 1898, of the Comité Consultatif des Arts et Manufactures. He was Foreign Fellow of the Royal Society of London; of our own Society; an honorary member of the Royal Institution, and of the Academies of Denmark, Vienna, Belgium, Upsala, Haarlem, Amsterdam, New York, and Turin, besides numerous others. He was also Commandeur de la Légion d'Honneur.

In 1887 the Institut awarded him the Prix Lacaze, one of its most valuable gifts; he was the Davy medallist in 1896, and the Hofmann medallist in 1903; and he obtained honours from the Franklin Institute of Philadelphia, from the Société d'Encouragement pour l'Industrie Nationale, and the Société Industrielle du Nord de la France; and in 1906, shortly before his death, he was awarded the Nobel Prize for Chemistry.

Moissan was a practised speaker and a perfect expositor. His lectures at the Sorbonne were crowded with enthusiastic students, all eager to catch every word, and he kept their attention for an hour and three-quarters at a time by a clear, lucid exposition, copiously illustrated by well-devised experiments. His command of language was admirable; it was French at its best; the charm of his personality and his evident joy in exposition gave keen pleasure to his auditors. He will live long in the memories of all who were privileged to know him, as a man full of human kindness, of tact, and of true love of the subject which he adorned by his life and work. Perhaps the key to his character lies in his own words: "Nous devons tous placer notre idéal assez haut pour ne pouvoir jamais l'atteindre;" or as our own poet has put it: "O but a man's reach should exceed his grasp; or what's a heaven for?"

LVI.—*The Triazo-group. Part XX. Azoimides of the Propane Series.*

By Martin Onslow Forster and John Charles Withers.

As a result of observing the refraction and dispersion of certain triazo-compounds, two principles among others were established by Philip (Trans., 1908, **93**, 918). In the first place, it could be stated that the increment in refraction or dispersion due to the N_3-group when united to singly-linked carbon is almost identical with the atomic refraction or dispersion of bromine in similar circumstances; and secondly, that the refraction increment for the N_3-group is considerably above this normal value when the carbon atom with which it is combined is unsaturated. This intensified influence of the triazo-group was illustrated by ethyl triazoformate, phenylazoimide, and α-naphthylazoimide, the refraction and dispersion of which were compared with those of ethyl triazoacetate, α-triazopropionate, β-triazopropionate and bistriazoacetate, also with those of triazoethyl alcohol, αβ-bistriazoethane, and benzylazoimide. The cause of this exaltation, however, remains unexplained, and as the matter is one of considerable importance in connexion with the supposed arrangement of atoms in the azoimide nucleus, it appeared desirable to collect fresh material for refractometric study.

The only known aliphatic azoimides in which the triazo-group is attached to unsaturated carbon are the triazoformic esters and vinylazoimide. Ethyl triazoformate was examined by Philip (*loc. cit.*), and revealed the peculiarity indicated, whilst vinylazoimide (Trans., 1910, **97**, 2570) is unsuited to the purpose on account of its low boiling point (26°/760 mm.). It seemed probable, however, that by applying the principles underlying the production of the last-named substance, we might arrive at αγ-bistriazopropylene, $N_3{\cdot}CH_2{\cdot}CH{:}CH{\cdot}N_3$, and αβ-bistriazopropylene,

$$N_3{\cdot}CH_2{\cdot}C(N_3){:}CH_2,$$

both of which substances contain one triazo-group attached to saturated, and one to unsaturated, carbon; moreover, they should be liquids boiling considerably higher than vinylazoimide. Another point in connexion with the optical effect of an azoimide nucleus invited attention to these materials. Vinylazoimide, $CH_2{:}CH{\cdot}N_3$, is yellow, although allylazoimide, $CH_2{:}CH{\cdot}CH_2{\cdot}N_3$, is colourless, and as the same peculiarity distinguishes diazoacetic ester from ethyl triazoacetate, it seemed worth while to ascertain how far the appearance of colour is to be associated with the triazo-group.

Setting out from αγ-dichlorohydrin, this was converted into

$\alpha\gamma$-bistriazo-*iso*propyl alcohol, in which the hydroxy-group was replaced by chlorine; $\alpha\gamma$-bistriazo-β-chloropropane,

$$N_3\cdot CH_2\cdot CHCl\cdot CH_2\cdot N_3,$$

was then deprived of the elements of hydrogen chloride, yielding $\alpha\gamma$-bistriazopropylene as a yellow liquid boiling at 74°/19 mm. Progress had been made in the preparation of the isomeride by the production of $\alpha\beta$-bistriazopropyl alcohol and $\alpha\beta$-bistriazo-γ-chloropropane, $N_3\cdot CH_2\cdot CH(N_3)\cdot CH_2Cl$, when the investigation was brought to an abrupt conclusion by a deplorable accident. A specimen of the $\alpha\gamma$-bistriazopropylene, which had been successfully examined in the refractometer by Dr. Philip, was being weighed for analysis, when it exploded spontaneously, inflicting serious injuries on one of us (J. C. W.).

Although the original programme could not be completed, there is a point in connexion with the work which it is worth while to place on record. Since triazoethyl bromide is conveniently obtained from triazoethyl alcohol and phosphorus tribromide, it was intended to use the last-named, in action with $\alpha\gamma$-bistriazo-*iso*propyl alcohol, to prepare the halogen derivative necessary for the production of $\alpha\gamma$-bistriazopropylene. The process, however, failed, owing to excessive production of a viscous, brown oil, analogous to that by-product which diminished the yield of triazoethyl bromide, but our attention was drawn to the appearance of ammonium bromide, formation of which seemed most likely due to the hydrogen bromide, liberated in the action, hydrolysing the azoimide nucleus. Accordingly, Mr. B. B. Dey examined the behaviour of other triazo-compounds towards hydrogen bromide in glacial acetic acid, and found that the production of ammonium bromide is quite a common feature with aliphatic azoimides, ethyl triazoacetate, for instance, yielding the bromoacetate and a very small proportion of amino-acetate, whilst triazoethyl alcohol gave bromoethyl acetate, the product in each case being associated with a large proportion of ammonium bromide; very little ammonium salt arises from aromatic azoimides, however, phenylazoimide yielding 2:4-dibromoaniline with traces of aniline and ammonia, the latter being obtained also from *p*-triazobenzoic acid in association with 3:5-dibromo-4-aminobenzoic acid. Mr. Dey's experiments were being continued, when a private communication from Professor Curtius informed us that he was engaged in somewhat similar work, and we have therefore abandoned it.

Subsequently it was found that the replacement of hydroxyl by chlorine in $\alpha\gamma$-bistriazo-*iso*propyl alcohol and in $\alpha\beta$-bistriazopropyl alcohol may be effected smoothly and regularly by the process of Darzens (*Compt. rend.*, 1911, **152**, 1314), in which thionyl chloride is substituted for phosphorus halide, and the liberation of halogen hydride is avoided by the presence of dimethylaniline.

Concurrently with the foregoing, an investigation of aliphatic triazo-amines, begun with the preparation of β-triazoethylamine (Trans., 1911, **99**, 1277), has been extended to those of the propane series. γ-Triazopropylamine has been obtained as a colourless oil, which boils at 56—57°/16 mm., and forms the usual carbamide derivatives with cyanic acid, phenylcarbimide, and phenylthiocarbimide, all of which melt lower than the respective derivatives of β-triazoethylamine. In spite of the fact that γ-triazopropylamine and β-triazoethylamine are stable materials, much difficulty has been encountered in preparing β-triazopropylamine; an aqueous solution of its salts undergoes decomposition during evaporation, and although a small quantity of the base was isolated in the form of a colourless oil boiling at 44—46°/16 mm., derivatives could not be obtained.

EXPERIMENTAL.

γ-*Triazopropylamine*, $N_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot NH_2$.

The γ-bromopropylamine hydrobromide was prepared by the method of Gabriel and Weiner (*Ber.*, 1888, **21**, 2673) from trimethylene dibromide and potassium phthalimide, the resulting γ-propylphthalimide being hydrolysed with hydrobromic acid. The salt (5·5 grams) and sodium azide (4 grams) in water (10 c.c.) were heated during six to seven hours on the steam-bath, when 10 c.c. of 20 per cent. sodium hydroxide were added to the dark, strongly-smelling liquid; steam distillation into dilute hydrochloric acid gave a clear solution, which did not yield crystals until completely evaporated in a vacuum desiccator, 90 per cent. of the amount required by theory being deposited. The hydrochloride is very hygroscopic, and after being dried over phosphoric oxide melted at about 90°. On adding solid potassium hydroxide to a concentrated aqueous solution, the whole quantity of base could be removed by several extractions with ether, the residue from this being distilled under reduced pressure over fresh alkali:

0·0885 gave 42·7 c.c. N_2 at 22° and 775 mm. $N = 55\cdot 98$.

$C_3H_8N_4$ requires $N = 55\cdot 99$ per cent.

γ-Triazopropylamine is a colourless, strongly basic-smelling liquid, and boils at 56—57°/16 mm. It is very soluble in water, and the effervescence with concentrated sulphuric acid or with stannous chloride in hydrochloric acid is very vigorous.

Reduction to Propylenediamine.—On adding a solution of stannous chloride in hydrochloric acid containing 0·5 gram of the metal to 0·5 gram of the hydrochloride in water, liberation of nitrogen took place immediately, and when this had ceased excess of alkali was added, followed by 2 grams of benzoyl chloride. The solid product, after crystallisation from hot benzene, melted at 143°, and gave $N=9{\cdot}72$ ($C_{17}H_{18}O_2N_2$ requires $N=9{\cdot}95$ per cent.), being thus identified with $\alpha\gamma$-dibenzoylaminopropane (Strache, *Ber.*, 1888, **21**, 2365).

γ-*Triazopropylcarbamide*, $N_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}NH_2$.

A concentrated solution of γ-triazopropylamine hydrochloride with the same quantity of potassium cyanate was allowed to evaporate to dryness in a vacuum desiccator, the residue being extracted with absolute alcohol; this left a yellowish-brown, crystalline mass, which was extracted with a considerable volume of hot benzene, and filtered, when colourless, pearly flakes separated, melting at 52°:

0·0676 gave 31·9 c.c. N_2 at 24° and 760 mm. $N=53{\cdot}17$.

$C_4H_9ON_5$ requires $N=53{\cdot}42$ per cent.

The carbamide is freely soluble in water and in alcohol, dissolving sparingly in benzene; it is insoluble in petroleum, and effervesces vigorously with concentrated sulphuric acid.

s-*Phenyl*-γ-*triazopropylcarbamide*,
$N_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_6H_5$.

When γ-triazopropylamine (1 gram) and phenylcarbimide (1·2 grams), both diluted with dry benzene, were mixed, a vigorous action took place and the temperature rose; the carbamide did not crystallise, however, until the colourless residue from the evaporated solvent was rubbed. After recrystallisation from a mixture of benzene and petroleum it melted at 60°:

0·0990 gave 27·7 c.c. N_2 at 24° and 773·6 mm. $N=32{\cdot}03$.

$C_{10}H_{13}ON_5$ requires $N=31{\cdot}96$ per cent.

The substance is freely soluble in alcohol, acetone, ether, or ethyl acetate, more sparingly so in benzene, and not at all in petroleum. The reaction with concentrated sulphuric acid is moderate, and an alcoholic solution effervesces with stannous chloride.

s-*Phenyl*-γ-*triazopropylthiocarbamide*,
$N_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_5$.

Although action took place immediately on mixing γ-triazopropylamine (1 gram) and phenylthiocarbimide (1·35 gram), both diluted with dry benzene, the thiocarbamide did not separate until petroleum was added to the concentrated solution; it melts at 59°:

0·1394 gave 36·4 c.c. N_2 at 25° and 769 mm. N = 29·68.

$C_{10}H_{13}SN_5$ requires N = 29·78 per cent.

The thiocarbamide is insoluble in petroleum, and is only moderately soluble in ether, benzene, or hot water, but is dissolved freely by alcohol, acetone, glacial acetic acid, or chloroform; the reaction with concentrated sulphuric acid is sluggish.

β-Triazopropylamine, $CH_3{\cdot}CH(N_3){\cdot}CH_2{\cdot}NH_2$.

The method of Uedinck (*Ber.*, 1899, **32**, 967) was employed in preparing β-bromopropylamine hydrobromide from allylthiocarbimide and hydrobromic acid. The salt was treated as in the production of the foregoing isomeride, but the resulting β-triazopropylamine hydrochloride was a dark brown material, which we could not purify, as it appears to undergo decomposition when the aqueous solution is evaporated under diminished pressure, even at laboratory temperature. The free base was isolated as before, but the yield was most disappointing, only 1·8 grams being obtained from 27·5 grams of β-bromopropylamine hydrobromide:

0·0858 gave 42·0 c.c. N_2 at 22° and 752 mm. N = 55·73.

$C_3H_8N_4$ requires N = 55·99 per cent.

β-Triazopropylamine is a colourless oil, boiling at 44—46°/16 mm.

Reduction to αβ-Diaminopropane.—The relationship of the triazo-base to the corresponding diamine was established by means of stannous chloride, the product being then benzoylated; the expected αβ-dibenzoylaminopropane, after crystallisation from benzene, melted at 188° (Strache, *loc. cit.*), and gave N = 9·97 ($C_{17}H_{18}O_2N_2$ requires N = 9·95 per cent.).

*αγ-Bistriazo*iso*propyl Alcohol*, $N_3{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}N_3$.

Fifty grams of αγ-dichlorohydrin (b. p. 80—85°/20 mm.) were heated on the steam-bath with 60 grams of sodium azide continuously during twelve days and nights in a flask protected from light, the brown mass being then transferred to a filter, and washed several times with ether; the latter having been dried with sodium sulphate was evaporated, and the residue fractionated under 0·6 to 1·0 mm. pressure. Three fractions were collected, of which the first was unchanged material, the second, boiling at 80—88°, consisting of α-triazo-γ-chloro*iso*propyl alcohol, whilst the bistriazo-derivative boiled above 88°; about 20 grams of each triazo-compound were formed, but if the 50 grams of starting material were made up from the two lower fractions, as much as 35 grams of bistriazo*iso*propyl alcohol would be produced.

The last-named substance is a colourless, odourless liquid, boiling at 88—91°/0·6 mm., and having D 1·2687/21°. Several attempts to estimate the nitrogen by combustion resulted in explosions, even when the material was diluted largely with copper oxide and volatilised very slowly; accordingly, it was necessary to measure the gas liberated by stannous chloride, with which vigorous effervescence takes place:

0·0716 gave 24·4 c.c. N_2 at 21° and 768 mm. N = 39·05.

$C_3H_6ON_6$ requires 2/3N = 39·43 per cent.

The bistriazo-compound acts violently with concentrated sulphuric acid, and explodes when subjected to percussion.

*α-Triazo-γ-chloro*iso*propyl Alcohol*, $N_3 \cdot CH_2 \cdot CH(OH) \cdot CH_2Cl$.

The intermediate fraction obtained in the isolation of bistriazo-*iso*propyl alcohol was found to be a colourless, odourless liquid, boiling at 83°/0·65 mm., and having D 1·3090/21·5°:

0·0887 gave 23·8 c.c. N_2 at 19° and 765 mm. N = 31·12.
0·3614 „ 0·3800 AgCl. Cl = 26·01.

$C_3H_6ON_3Cl$ requires N = 31·01; Cl = 26·16 per cent.

The substance is less dangerous than the bistriazo-compound, so that nitrogen could be estimated in the ordinary way, chlorine determinations being made by Stepanoff's method; nevertheless, there is vigorous action with concentrated sulphuric acid or with stannous chloride in hydrochloric acid.

αγ-Bistriazo-β-chloropropane, $N_3 \cdot CH_2 \cdot CHCl \cdot CH_2 \cdot N_3$.

As already stated, the first attempts to replace the hydroxyl group in αγ-bistriazo*iso*propyl alcohol were made with phosphorus tribromide, which was added to the alcohol in dry chloroform, when ammonium bromide was precipitated as a result of the liberation of hydrogen bromide; the residue from the chloroform solution consisted principally of a dark brown, viscous oil, from which a small quantity of a colourless, limpid, sweet-smelling liquid was distilled off at 68—74°/0·9 mm., and redistilled at 64°/0·55 mm. Analysis revealing 30 per cent. of nitrogen and 50 per cent. of bromine instead of 41 and 39 per cent. respectively, and the yield being very poor, the process was abandoned in favour of the one for replacing hydroxyl by chlorine quite recently described by Darzens (*loc. cit.*).

αγ-Bistriazo*iso*propyl alcohol (14·2 grams) was mixed with dimethylaniline (12·1 grams) in a flask provided with a dropping-funnel and a tube containing calcium chloride, thionyl chloride (12·5 grams) being added during fifteen minutes to the cooled and shaken liquid, which gradually became viscous, and changed in colour through green to dark brownish-red. On replacing the funnel and tube by an air condenser, and heating the product in steam, sulphur dioxide was liberated during thirty minutes, when the material was poured into cold water to dissolve dimethylaniline hydrochloride, and then extracted with ether; this was washed successively with 10 per cent. hydrochloric acid, 10 per cent. sodium carbonate, and water until neutral, dried with calcium chloride, and evaporated. The residue, weighing 13 grams, corresponding with 81 per cent. of the theoretical amount, boiled at 62—65°/0·6—0·8 mm.:

0·0711 gave 33·0 c.c. N_2 at 21° and 742 mm. N = 52·40.
0·2494 „ 0·2238 AgCl. Cl = 22·20.
$C_3H_5N_6Cl$ requires N = 52·35; Cl = 22·09 per cent.

αγ-Bistriazo-β-chloropropane is a colourless liquid, which becomes yellow on exposure to light; it has a slightly pungent, sweet odour, and acts vigorously with concentrated sulphuric acid. The substance boils at 63°/0·6 mm., and has D^{22} 1·3037.

αγ-Bistriazopropylene, $N_3{\cdot}CH_2{\cdot}CH{:}CH{\cdot}N_3$.

Forty grams of αγ-bistriazo-β-chloropropane were shaken during three hours with 200 c.c. of alcohol and 40 grams of potassium hydroxide dissolved in 50 c.c. of water, yielding a homogeneous, pale yellow liquid containing crystals of potassium chloride. After two days in darkness, when the crop of solid had greatly increased, a current of steam was passed through the alcohol, which was followed in the receiver by a pale yellow emulsion. The whole product was diluted in a separating funnel to 1000 c.c. with water, from which the yellow oil could be removed after four hours, a further quantity being obtained from the aqueous alcohol by saturating it with sodium acetate and extracting with ether.

Previous experiments having shown that the substance is sensitive to rise of temperature and undergoes gradual decomposition during distillation, the portion which had been tapped from the diluted steam-distillate, and which might be regarded as nearly pure, was dried by sodium sulphate and distilled, a middle fraction of 6 grams being taken at 72—74°/19 mm. for the purpose of analysis and refractometric examination. The remainder was mixed with the product of ether extraction, and after a very small quantity of a volatile, nearly colourless liquid had passed over, 10 grams distilled at 78—79°/26 mm., when crystals of ammonium azide were noticed in the condenser, and the low pressure could no longer be maintained. Unhappily, as already stated, the sequel to this experiment was most disastrous. An estimation of nitrogen was made by the combustion process without mishap, but as the result was somewhat low (63·2 per cent., instead of 67·7), in consequence probably of a too rapid liberation of gas, preparation was being made for repetition, when without warning the substance exploded with frightful violence.

αγ-Bistriazopropylene is a sulphur-yellow, mobile liquid, having a somewhat fishy odour, the vapour producing on inhalation the characteristic throbbing effect of the more volatile aliphatic azoimides. It explodes violently under percussion and with concentrated sulphuric acid.

αβ-Bistriazopropyl Alcohol, $N_3 \cdot CH_2 \cdot CH(N_3) \cdot CH_2 \cdot OH$.

The necessary αβ-dibromopropyl alcohol was obtained in 85 per cent. yield from allyl alcohol and bromine in carbon disulphide; it boiled at 96°/5 mm. or 100°/10 mm. Seventy grams were heated with 50 grams of sodium azide during thirteen to twenty days, the subsequent operations being the same as those followed in the case of αγ-bistriazo*iso*propyl alcohol; fractionation revealed a considerable proportion of the intermediate compound, but in later experiments, when this was included in the starting material, more than 70 per cent. of the theoretical yield was obtained. On reduction with stannous chloride:

0·0937 gave 32·0 c.c. N_2 at 21° and 763·6 mm. N = 38·87.

$C_3H_6ON_6$ requires 2/3N = 39·43 per cent.

αβ-Bistriazopropyl alcohol is a colourless, odourless liquid, boiling at 91—93°/0·7 mm., and having D^{21} 1·2609; the action with concentrated sulphuric acid is violent.

αβ-Bistriazo-γ-chloropropane, $N_3 \cdot CH_2 \cdot CH(N_3) \cdot CH_2Cl$.

Using the foregoing substance in place of αγ-bistriazo*iso*propyl alcohol, the procedure was exactly the same as in the preparation of the isomeride, a yield of 82 per cent. being obtained:

0·2391 gave 0·2158 AgCl. Cl = 22·28.

$C_3H_5N_6Cl$ requires Cl = 22·09 per cent.

αβ-Bistriazo-γ-chloropropane is a colourless oil with a very faint, sweet odour, and acting vigorously with sulphuric acid; it boils at 62°/0·6 mm., and has D^{21} 1·3322.

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LVII.—*The Action of Ozone on Cellulose.*

By Mary Cunningham and Charles Dorée.

The studies on the action of ozone on organic substances carried out in recent years by Harries and others have yielded results of great importance, even when applied to such complex naturally occurring materials as caoutchouc and Japan lac. The use of ozone for industrial purposes also is being rapidly extended, and among possible applications its employment for the bleaching of cotton and other cellulose yarns has recently again been suggested. It seemed to us, therefore, that an inquiry into the nature of the action of ozone on the celluloses might afford results of interest and possible utility. The present communication contains an account of some experiments made with this object, the first part dealing with cellulose (cotton), and the second with the lignocellulose, jute.

Part I.—The Action of Ozone on Cotton.

Kolb in 1868 exposed dry linen to the action of ozone for a week, and stated that the cellulose was attacked, and increased in weight (*Bull. Soc. ind. Mulhouse*, 1868, **38**, 94). Witz (*Bull. Soc. Rouen*, 1883, **11**, 198) found that, in the presence of water. cotton was converted into oxycellulose, since the product showed an increased affinity for methylene-blue. Vignon also, in the course of his researches on the oxycelluloses, mentions the formation of these derivatives by the action of ozone.

Experimental.

Pure bleached cotton-wool was used chiefly in these experiments. It was always, if possible, weighed without drying, the moisture being estimated in a duplicate sample. The ozonised oxygen contained 1·5 to 2 per cent. by weight of ozone (20 to 25 grams per cubic metre), and was delivered at the rate of 3 to 6 litres per hour. The cotton was sprayed with water, and suspended from glass hooks in tall calcium chloride towers. These were connected with absorption bottles containing barium hydroxide solution for the estimation of any carbon dioxide and volatile acids produced. The estimations of furfuraldehyde were made by the phloroglucinol method, and the results calculated from the tables given by Kröber (*J. Landw.*, 1901, **48**, 357).

The Action of Ozone on Cotton in the Absence of Water.

Five grams of cotton, dried at 110°, were ozonised for two hours. A small quantity of carbon dioxide was produced. The cotton had acquired a fatty odour, was acid to moist litmus paper, and at once liberated iodine from potassium iodide solution. This oxidising property was not affected by keeping the product in a vacuum for twenty-four hours, but on remaining in the air it weakened somewhat, and after two weeks' exposure it disappeared. The acidity could be removed by washing with tap water. When dried at 80° or above, the fibres turned brown, lost the power of liberating iodine, but continued acid. For comparison, a sample of the cotton was ozonised moist. The products were very similar, except that the iodide reaction was less strong and the acidity more pronounced.

The properties acquired by cotton as the result of a short exposure to ozone therefore show a very close resemblance to those observed by Cross and Bevan in the case of cotton and linen which had been bleached by chloride of lime, and washed without the use of an "antichlor" (*Zeitsch. angew. Chem.*, 1906, **19**, 2101). The liberation of iodine from potassium iodide was explained by these authors as due to the formation of a peroxide derivative of cellulose, which was stable under the ordinary conditions of industrial treatment. Since ozone acting on organic substances is known in many cases to form peroxides, the observations recorded above strongly support the view that the compound obtained in each case is a cellulose peroxide.

The Action of Ozone on Cotton in the Presence of Water.

Ozone of the concentration used rapidly attacked moist cotton. Brown, unbleached samples became white in one to two hours. When dried, the fibre was tendered and dusty. The evolution of carbon dioxide and the development of acidity in the fibre continued to increase with the time, and in order to gain some idea of the rate of the action, quantities equivalent to 2 grams of the dried cotton were ozonised under similar conditions for different periods. The unbleached cotton was in the form of loose wick, and was purified by washing with soap and water, and finally with alcohol and ether. The carbon dioxide was estimated by titration of the barium hydroxide solution with $N/20$-acid. The contents of the absorption bottle were washed out, steeped in boiled water for one hour, and the mixture titrated with $N/10$-sodium hydroxide, using phenolphthalein as indicator. After another hour additional alkali was added until the pink colour returned, and the total alkali used was regarded as equivalent to the acidity developed in the fibre. In some cases an additional quantity of cotton equivalent to 1 gram was ozonised in the same bottle, and used to determine the reducing power of the product towards Fehling's solution. Some of the results of these experiments are given in the following tables.

TABLE I.

Action of Ozone on Unbleached Cotton.

Concentration 1·4 per cent. Experimental values calculated to 100 grams of dry cotton.

Time in hours.	$N/10$-NaOH, c.c.	$N/10$-CO_2, c.c.	Copper reduced, grams.
2½	98	98	6·24
5	113	261	6·99

TABLE II.

Action of Ozone on Bleached Cotton.

Concentration 1·6 per cent. Experimental values calculated to 100 grams of dry cotton.

Time in hours	1	3	6	21
$N/10$-NaOH, c.c.	113	225	303	727
$N/10$-CO_2, c.c.	176	258	341	—

These numbers have no more than a relative value. The state of compactness of the cotton and its previous treatment greatly influenced the results, as is shown by the difference in the figures of tables I and II. The bleached cotton also under the conditions of titration absorbed 38 c.c. of the alkali per cent. In the case of the longer treatments the cotton-wool was pulled out at intervals to secure more uniform exposure. The results show that a considerable amount of action takes place even in one hour, and that the production of carbon dioxide is slightly greater than, but runs parallel to, the acidity developed in the fibre.

In order to examine more exactly the nature of the products formed, some experiments were made with larger quantities of cotton, two of which are given in detail.

Experiment A.—10·3 Grams of bleached cotton-wool containing 6 per cent. of moisture were sprayed with water, and ozonised in a subdued light for thirty hours in a wide horizontal tube. The cotton was disturbed and pulled out at intervals during this time. The concentration used was 1·4 per cent., and throughout the time the ozone remained in excess.

The residue was white, sensitive to light, and acid. When immersed in water it swelled up, filling the whole water space. The water digest was opalescent, and probably contained a little water-soluble oxycellulose. Moulds grew in it rapidly. On washing the fibre, neutral wash waters were soon obtained, but the fibre itself remained very acid. On drying at 100° it became of a light brown colour, and reacted acid when pressed on to moist litmus paper. The dried material disintegrated into a light, dusty powder. On boiling with water, or digesting with dilute ammonium or sodium hydroxide, it gave a pale yellow liquid. When boiled for ten minutes with 10 per cent. potassium hydroxide solution, a dark brown liquid was obtained, which on acidifying became lighter in colour, but only a trace of precipitate appeared on keeping. The loss of weight by this treatment, however, was 64·2 per cent. (1·436 dry at 105° left 0·5146.)

The ozonised fibre rapidly reduced Fehling's solution, but not ammoniacal silver solution (difference from hydralcellulose).

The estimations which follow were made with the brown residue left after washing several times with water and once with very weak ammonia, and drying at 105°. It was found subsequently that on steeping in dilute sodium hydroxide and washing with dilute acetic acid and water a residue was left which was neutral, and remained white at 105°.

(*a*) *Hygroscopic Moisture at* 110°.—7·45 per cent.

(*b*) *Methylene-blue Absorption.*—This was carried out by Vignon's method (*Bull. Soc. chim.*, 1901, [iii], **25**, 135).

One gram of the substance was boiled for ten minutes with 100 c.c. of a solution containing 0·06 gram of the dyestuff. The fibre was washed until the filtrate and washings amounted to 500 c.c. The lengths of equivalent colour columns of this liquid and of the original solution similarly diluted were compared.

The sum of three comparisons gave:

Length of standard : length of exhausted solution = 7·5 : 13·9.
Methylene-blue absorbed = 2·96 grams per cent.

(*c*) *Estimation of Furfuraldehyde.*—2·7765 gave 0·0537 furfuraldehyde-phloroglucide.

Furfuraldehyde found = 1·1 per cent.

(*d*) *Copper Number.*—The substance was boiled for fifteen minutes with Fehling's solution, the precipitate collected, washed, dried, and ignited. The residue was dissolved in 10 per cent. nitric acid, the solution filtered, and the copper determined by electrolysis:

1·8135 gave 0·2713 Cu.

Copper reduced = 14·96 per cent.

(*e*) *Elementary Analysis:*—

0·1736 gave 0·2772 CO_2 and 0·0982 H_2O. C = 43·55; H = 6·27.
$4C_6H_{10}O_5 + C_6H_{10}O_6$ requires C = 43·58; H = 6·05 per cent.
$3C_6H_{10}O_5 + H_2O$ requires C = 43·64; H = 6·26 per cent.

Experiment B.—10·1 Grams of the bleached cotton-wool containing 6·5 per cent. of moisture were ozonised as before for twenty-four hours.

The product was white and acid. It was found that the acidity could be removed by boiling with water, so that in this case the whole of the ozonised fibre was distilled in a current of steam for two hours.

(i) The *distillate* was faintly acid, due probably to a trace of acetic acid, since it gave a red colour with ferric chloride. It did not reduce Fehling's solution. It was opalescent, and full of minute, floating particles, some of which under the microscope appeared to be crystals in the form of oblong plates.

(ii) The *water digest*, from which the fibre had been filtered off, was pale yellow, acid, and possessed powerful reducing properties. It was neutralised with sodium hydroxide, evaporated to dryness, and the furfuraldehyde in it estimated by distillation with hydrochloric acid:

0·0662 gram of furfuraldehyde-phloroglucide, equivalent to 0·037 gram of furfuraldehyde, was obtained.

This represents 0·4 per cent. of furfuraldehyde calculated on the original weight, 9·44 grams of dry cotton taken, or 3·4 per cent. on the soluble portion, assuming that this is represented by the difference between the original weight taken and that of the residue left after the ozone and water treatment.

(iii) The *residual fibre* was white and neutral. After drying at 105°, it showed no sign of discoloration, and weighed 8·35 grams, or 88·4 per cent. of the original. The loss in weight due to the treatment is therefore 11·6 per cent. Separate portions of the dried fibre were taken, and the following estimations made:

1·456 gave 0·0379 furfuraldehyde-phloroglucide. Furfuraldehyde = 1·54 per cent.
2·775 gave 0·4681 Cu. Copper reduced = 16·86 per cent.
0·2144 „ 0·3419 CO_2 and 0·1188 H_2O. C = 43·47; H = 6·17 per cent.

These results are collected in the following table. Corresponding values for the cotton used, determined by the same methods, are included. For comparison, the constants of an oxycellulose made by Vignon (*Bull. Soc. chim.*, 1898, [iii], **19**, 790) by the action of hydrochloric acid and potassium chlorate, and another, prepared by

Faber and Tollens (*Ber.*, 1899, **32**, 2592) by the action of bromine water in the presence of chalk, are also given.

TABLE III.

	Original cotton.	Product *A*. Ozone 30 hours, brown.	Product *B*. Ozone 24 hours, white.	Oxy-cellulose. $KClO_3 + HCl$ yellow (Vignon).	Oxy-cellulose. Bromine water (Tollens)
Yield per cent.	—	—	88·4	—	85—88
Composition C	44·44	43·55	43·47	43·55	42·29
,, H	6·17	6·27	6·17	6·03	6·15
Moisture.....................	6·0	7·45	—	—	—
Furfuraldehyde	0·62	1·10	1·54	1·8	1·6
Methylene-blue	0·56	2·96	—	0·6	—
Copper number..	—	14·96	16·86	—	—
Loss in 10 per cent. KOH	—	64·2	—	87·6 *	—

* After fusion.

Ozone, therefore, converts cellulose partly into acidic derivatives which are easily soluble in dilute alkalis, and contain groups yielding furfuraldehyde, and partly into an insoluble substance which functions as an oxycellulose. The products are thus very similar to those obtained by Ditz (*Chem. Zeit.*, 1907, **31**, 844, 857) by the action of ammonium persulphate. These he describes as a cellulose peroxide, a free acid (? acid cellulose), and a reducing substance (probably oxycellulose). He regards the formation of the peroxide as due to the action of the oxidising agent on the aldehydic oxycellulose formed in the first instance. The products are not the same as those obtained by the action of hydrogen peroxide, which according to Bumcke and Wolffenstein yields hydralcellulose (*Ber.*, 1899, **32**, 2493), a substance of very marked aldehydic character. In keeping with this, these authors found that treatment with alkali resolved hydralcellulose into cellulose (alcohol) and an acid derivative. They regard the formation of oxycellulose as due primarily to hydrolysis, and not to oxidation (*Ber.*, 1901, **34**, 2415), their explanation being thus opposed to the "Celloxin" theory of Tollens (*Ber.*, 1901, **34**, 1436). In the case of ozone, if hydrolysis takes place, hydrogen peroxide must presumably be formed in the first instance. This is not altogether impossible, since it has been shown that in certain cases, in the absence of water, ozone causes an elimination of water from organic substances with subsequent action. It is difficult to imagine, however, that the action of ozone stops at hydrolysis, and that its powerful oxidising properties do not determine the final products obtained. It will be seen, by comparison with the two oxycelluloses prepared by widely different methods by Vignon and Tollens, that ozone converts cotton into a very similar derivative.

Methods at present available do not allow of any sharp differentiation of the oxycelluloses, either from one another or from allied substances, as they cannot be separated from unchanged cellulose, and no very characteristic properties have been observed.

Part II.—Action of Ozone on Jute (Lignocellulose).

The jute fibre may be considered as a complex composed of (1) 65 per cent. of a resistant α-cellulose, (2) 15 per cent. of a less resistant β-cellulose, which yields on distillation with condensing acids half its weight of furfuraldehyde; (3) 20 per cent. of a group of a quinonoid character, which yields no furfuraldehyde—the lignone group.

The mode in which these constituent groups are united together is not known. The cellulose when isolated by various treatments is obtained as oxycellulose. The lignone group possesses an unsaturated character combining directly with chlorine, and it was therefore thought not unlikely that ozone might also form a compound with this group of an ozonide or peroxide nature, the decomposition of which might throw some light on the character of the lignone complex.

The jute used in these experiments was not purified by a preliminary alkaline treatment. The cleanest and whitest portions of the fibre were selected, and to remove fatty matter these were extracted, air-dry, in a Soxhlet apparatus with ether for a week. The weights given in each case are calculated for fibre dry at 105—110°, but unless otherwise stated the fibre used for experiment was not dried. The method of experiment was similar to that described under cotton.

The Action of Ozone on Jute in the Absence of Water.

(*a*) 1·896 Grams of jute previously extracted with ether and dried at 105° were exposed to the action of ozone of 1·5 per cent. concentration. The fibre gradually became lighter in colour, and a small quantity of carbon dioxide was evolved. After five hours the weight was 1·94 grams. The fibre was greyish-white, and gave a slightly acid reaction when pressed on litmus paper. When boiled for five minutes in 1 per cent. sodium hydroxide solution, the loss in weight was 12·4 per cent. A duplicate sample of jute weighing 4·34 grams, when treated similarly, except that it was not exposed to the ozone, left 3·925 grams, showing the normal loss of 9·4 per cent.

(*b*) The 3·925 grams of dry jute obtained above were exposed for ten hours to the stream of ozone, the carbon dioxide produced being received in barium hydroxide solution. The weight of the jute remained unaltered. On titrating the barium hydroxide solution, a production of carbon dioxide equivalent to 12 c.c. of $N/20$-acid was observed. The 3·925 grams of ozonised fibre were boiled for five minutes in 1 per cent. sodium hydroxide solution, and left 3·705 grams—a loss of 5·6 per cent. A duplicate sample of jute which had been boiled for five minutes with 1 per cent. sodium hydroxide solution was dried, and again treated with the alkali for five minutes. The loss in this case was 2·8 per cent.

These experiments show that, in the absence of water, ozone has but little action on jute. Its colour was only slightly improved, and its strength apparently unaltered. A marked increase in weight pointing to the formation of an ozonide was not observed. The fibre, however, acquired the property of oxidising potassium iodide solution, so that traces of a peroxide were probably formed. This substance was decomposed by heating to 80°. Instead of combination with the jute a slight oxidation takes place, with the production of acid derivatives, as shown by the acidity of the fibre and its increased solubility in dilute alkali.

Several experiments were made in which the finely chopped dried jute was suspended in light petroleum, and the ozonised gas passed through the liquid. Again no direct combination with ozone was noticed. The fibre gradually became brown in colour, and carbon dioxide was evolved. The fibre after repeated washings with light petroleum and drying at 60° remained moist and acid. The acid substance could only be removed by prolonged digestion with dilute alkali, after which a typical product (brown after drying at 110°) had the composition $C=45·4$; $H=6·1$ per cent., and properties similar to those of the residues described below.

The Action of Ozone on Jute in the Presence of Water.

The fibre bundles were pulled out loosely, sprayed with water, and suspended in a large calcium chloride tower. On passing the current of ozonised gas, an immediate evolution of carbon dioxide was observed. At the same time the fibre became strongly acid, and began to bleach, except in a few places, which became of a deep golden-brown colour. In a few hours the fibre appeared almost uniformly white, but was very acid and tender. After a time, varying with the quantity of jute taken, the lignin reactions with phloroglucinol and with aniline acetate were no longer given. If exposed further to the ozone stream, the fibre gradually turned brown, and disintegrated. The fibre after treatment was very thin and weak. It had an odour somewhat resembling that of butyric acid, and this was found to be due to the presence of volatile acids which were slowly evolved. Washing with water failed to remove the acidity. Neutral wash waters could be obtained, but the fibre still showed an acid reaction. The acidity remained after drying at 105°, but by treating the fibre with very dilute sodium hydroxide or ammonia solution and then washing with water, a non-acid residue could be obtained.

As the oxidising action of the ozone, as evidenced by the evolution of carbon dioxide, was found to continue for a very long time, it was decided in the first place to measure the carbon dioxide, acidity, and loss of weight produced per hour, and secondly, to allow the action to continue until the lignin reactions were abolished (a fairly definite stage in the oxidation), and then to examine the alterations produced in the constituent groupings of the fibre, with the view of ascertaining the manner in which the oxidation had taken place.

The Progressive Action of Ozone on Moist Jute.

A series of experiments was made, as nearly as possible comparable, in which small quantities of jute were treated in the moist state for varying periods. The acidity developed was neutralised by *N*/10-alkali, as described under cotton, and the fibre residue weighed after washing with dilute acetic acid and water, and drying at 105°. The results obtained in this way are given in the following tables, experiments 1—5. Experiment 6 was made with a sample of jute "purified" by boiling for five minutes in 1 per cent. sodium hydroxide solution. It was washed and ozonised without drying. A duplicate experiment showed that the loss due to the alkaline treatment was 9·4 per cent., and from this value the weight of fibre ozonised, 3·27 grams, was calculated. Experiment 7 was made on a sample of jute cellulose isolated by chlorination. The yield of cellulose obtained in this case was 73·7 per cent. No. 8 contains the values for bleached cotton previously given.

TABLE IV.

Progressive Action of Ozone: Observed Values.

Ozone concentration 1·6 per cent., 5 litres per hour.

Expt.	Weight of dry jute.	Time in hours.	*N*/10-Sodium hydroxide, c.c.	Carbon dioxide as *N*/10-acid, c.c.	Total acidity.	Weight of fibre residue.
1	2·57	1	12·7	3·7	16·4	2·38
2	2·12	3	29·8	23·8	53·6	1·66
3	2·40	6½	48·0	55·5	103·5	1·81
4	2·79	10	68·5	75·0	145·5	2·00
5	2·54	13	75·1	83·0	158·1	1·73
6	3·27	5	80·0	—	—	2·43
7	3·45	12	5·6	36·6	42·2	3·14

TABLE V.

The Figures of Table IV Calculated to 100 *grams of Dry Jute.*

Expt.	Time in hours.	N/10-Sodium hydroxide, c.c.	CO_2 as N/10-acid, c.c.	Total acidity.	CO_2 weight per cent.	Fibre loss in weight.	Phloroglucinol reaction.
1	1	493	146	639	0·32	7·5	Bright
2	3	1406	1123	2529	2·47	21·7	Dull
3	6½	2000	2312	4312	5·09	24·6	Weaker
4	10	2451	2684	5135	5·81	28·3	,,
5	13	2957	3268	6225	7·19	32·0	None
6	5	2447	—	—	—	25·7	—
7	12	163	1061	1224	2·33	9·0	—
8	6	303	341	644	0·75	—	—

These numbers when plotted on a diagram showed:

(*a*) That the loss of weight undergone by the jute is uniformly rapid in the first three hours, the average loss being 7·5 per cent. per hour. In the succeeding ten hours the loss is slow, amounting in all to 11·3 per cent., but the rate of loss is constant, being about 1·13 per cent. per hour.

These results apparently indicate that at first one group of the complex, no doubt the lignone group, is attacked more rapidly than the others, but that when the loss has reached 22 per cent. the ozone attacks the residue more uniformly.

(*b*) The amount of alkali required to neutralise the acid produced shows a similar rapid and uniform increase in the first three hours, the average rate being 468 c.c. per cent. per hour. It then also becomes slower, but continues uniform at 155 c.c. per hour from the third to the thirteenth hour.

(*c*) The quantity of carbon dioxide produced increases during the first five hours, the average rate being 400 c.c. (as N/10-acid) per hour. It then becomes slower and apparently uniform at 158 c.c. per hour.

(*d*) The effect of a preliminary alkaline treatment is shown in experiment 6; 2447 c.c. of N/10-alkali were required to neutralise the acidity produced in five hours, whereas with untreated jute in the same time only 1710 c.c. were required. The alkali-treated jute is therefore very much more reactive to ozone than the untreated, as would be expected from the hydrolytic treatment to which it had been exposed.

(*e*) Experiment 7, on the cellulose isolated from jute by chlorination, shows that this cellulose is comparatively resistant. The loss of weight was 9·06, the alkali required 163 c.c., and the carbon dioxide equivalent to 1061 c.c., the corresponding figures for jute being 29, 2800 c.c., and 3000 c.c. Since the total acidity produced is so much greater in the case of jute than it is with the *α*- and β-cellulose constituent, it follows that it is the lignone group which is primarily attacked and oxidised.

The Action of Chlorine on the Ozonised Fibre.

The reactions with phloroglucinol, etc., formerly held to indicate the presence of the lignone group have been shown by Cross and Bevan (*Ber.*, 1901, **33**, 3132) to be due probably to traces of hydroxyfurfuraldehyde. This may be removed without materially affecting the lignone complex. After benzoylation by the Schotten-Baumann method also, the derivative no longer gives the lignin reactions, although the lignone group remains unaltered, and combines freely with chlorine (Cross and Bevan, "Researches on Cellulose," 1895–1900). The presence of hydroxyfurfuraldehyde is attributed to "natural" oxidation of the lignone group. In the case of ozone, therefore, a progressive development of hydroxyfurfuraldehyde would not be improbable, and if so the lignin reactions would cease only when the whole of the lignone had been oxidised, and their disappearance would mark a fairly definite stage in the action of ozone on the fibre. This certainly appears to be the case, as will be seen from the following experiments:

(*a*) 2·73 Grams of jute were ozonised for three hours, and treated with alkali, as in table V, 2. A loss of 22 per cent. would be expected, which might point to the removal of the lignone group. The fibres gave a fairly bright phloroglucinol reaction, however, and without drying were chlorinated for thirty minutes. The brown colour of the lignone chloride developed faintly, and a dull majenta was shown by the usual treatment with sodium sulphite. The residual cellulose weighed 1·84 grams, or 67·4 per cent. The lignone group has not been removed by the three hours' treatment, and the lignin reactions are still shown.

(*b*) In this case 4·67 grams were ozonised until the lignin reactions ceased. No reaction with chlorine could be observed, and the magenta tint did not develop with sodium sulphite. The cellulose isolated in the usual way weighed 3·04 gram, or 65 per cent.

(*c*) For comparison, a sample was ozonised as in (*b*), but not chlorinated. After neutralising with dilute alkali, washing, and drying, 66 per cent. of fibre residue was obtained.

These observations show that the lignin reactions and the removal of the lignone group apparently follow a parallel course.

Variation in the Furfuroid Constituents.

The jute used for experiment yielded 8·85 per cent. of furfuraldehyde. After treatment with ozone until the phloroglucinol reaction had ceased, this was reduced to 7·0 per cent.

5·27 Grams were ozonised, and without washing distilled with hydrochloric acid; one-half of the distillate gave 0·3545 gram of furfuraldehyde-phloroglucide.

On the assumption that no development of furfuraldehyde-yielding groups takes place in the course of the oxidation, this result shows that only some 2 per cent. of the furfuraldehyde, or one-quarter of the furfuraldehyde-yielding complex, is attacked by ozone, but that the properties of the β-cellulose group are profoundly modified, is proved by its solubility in very weak alkaline solutions, as shown by the following experiments.

Nature of the Fibre left after Removal of the Acidic Substances.

In the following experiments the acidic substances produced were removed in three ways:

(*a*) *By* N/10-*Sodium Hydroxide:*—2·30 Grams of jute were ozonised for five hours, after which time the phloroglucinol reaction ceased. The contents of the absorption bottle were allowed to steep in water. *N*/10-Sodium hydroxide solution was added until the liquid was neutral, 88 c.c. being required. The fibre was washed with water and very dilute acetic acid, and dried at 110°. (Residue, 1·44 grams, or 62·6 per cent.)

The fibre was white, and resembled cotton-wool. Treated with 10 per cent. sodium hydroxide solution, it gave no colour in the cold, and on heating only a pale yellow solution was obtained, the bulk remaining insoluble. On acidifying the alkaline liquid, a faint white precipitate was given. With concentrated sulphuric acid the fibre darkened, and dissolved to a brown solution. It absorbed and fixed methylene-blue, and reduced Fehling's solution. After drying at 110°:

0·1492 gave 0·2397 CO_2 and 0·0861 H_2O. C=43·81; H=6·41.
$(C_6H_{10}O_5)_8+H_2O$ requires C=43·84; H=6·24 per cent.

The yield of furfuraldehyde was 4·76 per cent., or 2·96 per cent. calculated on the original weight of jute taken. The filtrate and washings obtained after neutralisation were evaporated to dryness. This residue gave 0·0964 gram of furfuraldehyde-phloroglucide, representing 2·3 per cent. of furfuraldehyde calculated on the original weight of jute. Total furfuraldehyde found = 5·26 per cent. The original jute used in this and the next experiment gave 7·8 per cent.

(*b*) *By* N/10-*Ammonia:*—3·40 Grams of jute were ozonised with sample (*a*), and for the same time. The fibre was then suspended in water, and the ammonia solution added until the liquid remained faintly alkaline, an excess of ammonia being shown by the development of a yellow colour.

Weight of fibre residue dried at 110° = 2·287, or 67·3 per cent.

On analysis, 0·1644 gave 0·2641 CO_2 and 0·0950 H_2O. C = 43·81; H = 6·42 per cent.

Furfuraldehyde = 5·77 per cent, or 3·95 per cent. on the original weight of jute taken. (1·4064 gave 0·1513 of furfuraldehyde-phloroglucide.)

The filtrate and washings were evaporated to dryness, and left a brown mass having an odour of caramel. This gave on distillation 0·0902 gram of furfuraldehyde-phloroglucide, equivalent to 1·45 per cent. of furfuraldehyde calculated on the original weight of jute. Total furfuraldehyde found = 5·4 per cent., or 2·4 per cent. less than the original jute.

(*c*) *By Digestion with Water:*—27·12 Grams of jute were ozonised as before until the lignin reactions ceased. The fibre was then covered with water, and a current of steam passed through until acids no longer distilled over. This required seven hours. The liquid remaining in the flask was brown, and acid. The fibre was freed from acid by copious washing, and after drying at 105° weighed 19·84 grams, or 73·1 per cent.

This fibre, when boiled for five minutes in 1 per cent. sodium hydroxide solution, lost 16·9 per cent., and 45·8 per cent. of its weight in 10 per cent. sodium hydroxide. Its methylene-blue absorption was 1·5 grams per cent.

These results are collected in the following table:

TABLE VI.

Results obtained with the Fibre left after Treatment with Ozone until the Lignin Reactions disappeared.

	Original jute.	(*a*) Ozone and *N*/10-NaOH.	(*b*) Ozone and *N*/10-NH_4OH.	(*c*) Ozone and water at 100°.
Residue	100·0	62·6	67·3	73·1
Loss in weight	—	37·4	32·7	26·9
Composition C	46·5	43·81	43·81	—
,, H	6·0	6·41	6·42	—
Furfuraldehyde:				
(*a*) In fibre	—	2·96	3·95	—
(*b*) In solution	—	2·30	1·45	—
Total furfuraldehyde	7·8	5·26	5·40	—
"Loss" of furfuraldehyde	—	2·54	2·40	—

These results show that the loss of weight of the ozonised fibre and the amount of the furfuraldehyde-yielding constituents which passes into solution increase with the strength of the base used, The elementary composition of the fibre residue is the same, whether sodium hydroxide or ammonia is used for neutralising the acidity. The figures found, namely, $C = 43{\cdot}8$; $H = 6{\cdot}4$, agree closely with those required by the formula $(C_6H_{10}O_5)_8 + H_2O$, namely, $C = 43{\cdot}84$; $H = 6{\cdot}24$ per cent. This formula has been given by Bumcke and Wolffenstein to their hydralcellulose prepared from cellulose by the action of hydrogen peroxide (*loc. cit.*). The furfuraldehyde obtained after treatment is less by some 2·5 per cent. than that given by the original jute, so that a considerable modification of the β-cellulose grouping must have taken place. In its composition, furfuraldehyde-content, solubility in alkalis, its reactions with methylene-blue and with Fehling's solution, the fibre residue resembles the oxycelluloses.

The Acid By-products of the Oxidation.

Quantities of 20 to 30 grams of the moist ozonised fibre were suspended in water, and submitted to steam distillation. The liquid remaining in the flask was brown, and contained non-volatile acids. The distillate containing the volatile acids showed minute, floating crystals, but in quantity too small for isolation. It was neutralised with sodium or barium hydroxide, and after evaporation, qualitative tests showed the presence of acetic and formic acids. The reactions characteristic of formic acid with silver nitrate, ferric chloride, mercuric oxide, etc., were easily obtained. Acetic acid was identified, after the removal of the oxidisable acids by treatment with potassium permanganate, by the cacodyl oxide test and the preparation of its silver salt. The formic acid was estimated in the presence of the acetic acid by Fincke's method (*Apoth. Zeit.*, 1910, **25**, 727), in which the calomel produced by the reduction of mercuric chloride is weighed.

The following are brief details of the experiments made: (*a*) The 27·12 grams of jute used in the experiment described on p. 509 gave, on distillation in steam, volatile acid requiring 150·5 c.c. of $N/10$-sodium hydroxide to neutralise it. This is equivalent to 3·3 per cent. of acetic acid.

(*b*) Twenty-one grams of jute were ozonised moist until the lignin reaction became faint. The contents of the bottle were then digested with cold 1 per cent. sodium hydroxide solution. The fibre after washing with water was neutral, and weighed 16·3 grams. Loss of weight, 22·4 per cent. The alkaline liquid was acidified with sulphuric acid, and distilled in a current of steam. The volume of the distillate was 4·45 litres, and it required 189·1 c.c. of $N/10$-sodium hydroxide solution to neutralise it, equivalent to

5·4 per cent. of acetic acid. The solution of the sodium salts was concentrated, acidified, and the volatile acids distilled off, and made up to 500 c.c.:

100 c.c. gave 0·2089 Hg_2Cl_2, equivalent to 0·0204 formic acid.
100 c.c. required 12·43 c.c. $N/10$-NaOH.

The formic acid thus amounts to 35·6 per cent. of the total volatile acid.

(*c*) 15·74 Grams of jute were treated as in (*a*). The fibre residue weighed 13·17 grams; loss of weight = 16·3 per cent. The total volatile acid obtained required 66·0 c.c. of $N/10$-alkali:

50 c.c. of the acid liquid gave 0·1102 Hg_2Cl_2, equivalent to 0·0108 formic acid.

50 c.c. required 4·2 c.c. of $N/10$-sodium hydroxide solution.

The formic acid in this case represents 55·7 per cent. of the volatile acid. These results are collected below.

TABLE VII.

The Volatile Acids from Jute.

Expt.	Weight of jute.	Loss of weight per cent.	Volatile acidity $N/10$-alkali c.c. per cent.	Total acid, as acetic acid, formed.	Formic acid per cent. of total acid.
(*a*)	27·12	27·0	555	3·3	—
(*b*)	21·00	22·4	900	5·4	35·6
(*c*)	15·74	16·3	421	2·5	55·7

The liquid containing the non-volatile acids was golden-yellow. On being rendered alkaline, it turned brown. Moulds grew in it very rapidly. It instantly reduced silver nitrate and permanganate solutions and Fehling's solution after some time in the cold. It gave a precipitate with lime-water insoluble in acetic acid, which decolorised permanganate solution on warming, and appeared to be calcium oxalate. The quantity, however, was very small. In experiment (*b*) above only 0·8 per cent. of oxalic acid was found. From the filtrates amorphous calcium and barium salts were precipitated on the addition of alcohol, but in an impure condition, and their further examination led to no definite results.

Summary and Conclusions.

(1) Ozone up to 2 per cent. concentration at once attacks dry cotton, with the formation of a cellulose peroxide and an acid derivative.

(2) The peroxide is insoluble in water, is stable at the ordinary temperature, but is decomposed at 80°. The acidic substance is

insoluble in water, but is neutralised and removed by ordinary hard water. It contains furfuraldehyde-yielding groups.

(3) When boiled with water or digested with alkali, the acid derivative passes into solution, leaving a neutral product, which closely resembles the typical oxycelluloses.

(4) The industrial method of bleaching with ozone used on the Continent involves alternate treatment with dilute ozone and with bleaching powder solution. The latter would decompose the peroxide, and the acid derivative present would increase the activity of the bleach. As the results show, however, oxycellulose would be produced in proportion to the ozone action, with consequent weakening of the fibre.

(5) Whether the formation of peroxide and acid takes place simultaneously, or whether the former is produced from the aldehydic oxycellulose which may be formed in the first instance, is difficult to determine. The question has been discussed by Ditz (*J. pr. Chem.*, 1908, [ii], **78**, 343) in his work on the action of ammonium persulphate on cotton. If cotton-cellulose has the ketonic structure assigned to it by some authors, it may be that an atom of oxygen is fixed at the carbonyl group.

(6) In the presence of water, jute is oxidised with the formation of carbon dioxide. The fibre becomes acid, and the acid derivative is eliminated on hydrolysis with boiling water or with alkalis, with the formation of acetic and formic acids and complex non-volatile acids. The residual fibre is neutral, and has the properties of an oxycellulose of high furfuraldehyde-content.

(7) The ozone, whilst mainly attacking the lignone complex, to a less extent attacks the α- and β-cellulose groups.

(8) With ozone of about 2 per cent. concentration the action is rapid in the first three hours, subsequently becoming slower but uniform.

(9) The ozonised fibre shows the properties of an unstable peroxide rather than those of an ozonide. Its slow decomposition on boiling with water with the formation of formic acid resembles, however, the behaviour of certain complex ozonides.

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LVIII.—*The Catalytic Action of Copper at* 300° *on Some Alcohols of the Terpene Group.*

By George Ballingall Neave.

Sabatier and Senderens showed (*Bull. Soc. chim.*, 1905, [iii], **33**, 263) that when the vapours of some alcohols are passed over finely divided copper at a temperature of 300°, primary alcohols are decomposed into hydrogen and aldehydes, secondary alcohols into hydrogen and ketones, and tertiary alcohols into water and unsaturated hydrocarbons. Other alcohols were examined by the present author (*Analyst*, 1909, **34**, 346), and all were found to conform to the rule. This reaction therefore provides a convenient method for distinguishing between primary, secondary, and tertiary alcohols.

The behaviour of cyclic alcohols under these conditions seemed to the author to be worth investigation, and the following seven alcohols of the terpene group were examined: borneol, fenchyl alcohol, menthol, terpineol, terpin, *iso*borneol, and sobrerol.

The first three, which are regarded as secondary alcohols, yielded the ketones, camphor, fenchone, and menthone respectively. The tertiary alcohols terpineol and terpin were converted into dipentene. *iso*Borneol, the constitution of which is still considered doubtful, was converted to some extent into camphene, and must therefore, on the evidence furnished by this test, be considered a tertiary alcohol. Sobrerol, which contains both a secondary and a tertiary alcoholic group, was expected to yield the unsaturated ketone, carvone. Ring formation with loss of water, however, occurred, the product being pinol.

Experimental.

The copper was contained in a Jena-glass tube about 80 cm. long, heated in a cylindrical air-bath, and was prepared by the reduction of finely-powdered copper oxide at 300° by means of hydrogen which had been purified by passing it (1) through concentrated sulphuric acid, (2) over a heated copper spiral, and (3) over solid potassium hydroxide.

Borneol.—The borneol obtained from Messrs. Schimmel & Co., Leipzig, showed in alcoholic solution $[\alpha]_D^{20} + 37\cdot70°$ ($c = 18$). Ten grams were very slowly distilled over the copper at 300°, and 9 grams of a product melting at 180—181° were obtained. In alcohol this gave $[\alpha]_{D}^{20}$ $-41{\cdot}45^\circ$ ($c=20{\cdot}13$), and was evidently nearly pure *l*-camphor. The oxime prepared according to Auwers' method (*Ber.*, 1889, **22**, 605) melted at 120°.

Fenchyl Alcohol.—This compound, prepared by reducing fenchone by means of sodium and moist ether, melted at 41—42°, and was shown to be free from ketone. The product which was obtained by distilling it over the heated copper was a liquid which formed an oxime melting at 159—161°, and was therefore fenchone.

Menthol.—This was supplied by Kahlbaum. The product of the reaction was a liquid, but on keeping overnight, some crystals separated. The solid was shown to be unchanged menthol. The liquid, after removal of the crystals, boiled at 203—205°. It formed a semicarbazone melting at 183—184°, and a bromine derivative, m. p. 79—80°, and was therefore identified as menthone.

Terpineol.—This was obtained from Schimmel & Co., and was optically inactive. After distillation over copper in the usual way, there was collected a liquid, which was dried over sodium, and distilled in a current of carbon dioxide. The main fraction boiled at 176—179°, and consisted of dipentene. The tetrabromide and dihydrochloride were prepared according to the methods given by Perkin (Trans., 1904, **85**, 669). The former melted at 122—124°, the latter at 48—50°. The figures quoted by Perkin are 125° for the tetrabromide, and 48—50° for the dihydrochloride.

Terpin.—Terpin hydrate obtained from Kahlbaum was used. On distillation of this over copper, a product consisting of two layers was collected, the lower layer being water. The upper layer was separated, dried over sodium, and distilled in a current of carbon dioxide. The main fraction, boiling at 175—179°, was dipentene. The tetrabromide melted at 121—123°.

iso*Borneol.*—This compound, supplied by Schimmel & Co., was only slightly lævorotatory. By distilling it over copper in the usual way, there was obtained a white, crystalline solid, which consisted mostly of unchanged *iso*borneol, but on fractional precipitation from alcoholic solution by means of water, a small quantity of camphene, melting at 49—51°, was obtained.

Sobrerol.—The sobrerol, kindly supplied for this investigation by Professor Henderson, had been prepared by the action of mercuric acetate on pinene (Henderson and Agnew, Trans., 1909, **95**, 289). After distillation over copper in the usual manner, there was collected a liquid, which formed no oxime or semicarbazone, but which readily yielded a bromine derivative melting at 92—93°. This was shown to be pinol dibromide. The product of the reaction was therefore pinol.

In conclusion, I desire to express my thanks to Professor Henderson for the interest he has shown during the progress of this investigation.

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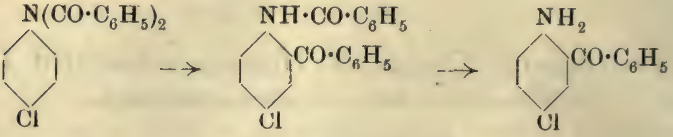
LIX.—*Isomeric Change of Halogen-substituted Diacylanilides into Acylaminoketones.*

By Andrea Angel.

It has already been shown (Chattaway, Trans., 1904, **85**, 386) that at somewhat high temperatures and under the influence of a catalyst, diacylanilides readily undergo rearrangement into acylaminoketones, the migrating acyl group invariably replacing a hydrogen atom in the para- or ortho-position with respect to the amino-group. It has further been shown (Chattaway and Lewis, Trans., 1904, **85**, 589) that when the para-position is already occupied by an alkyl group, as in dibenzoyl-*p*-toluidine, the migrating acyl group always enters the ortho-position with respect to the amino-group. The effect of a negative substituent such as chlorine or bromine in the para-position has not so far been investigated. Preliminary experiments by the first-named author on the transformation of the dibenzoyl derivatives of *p*-chloro- and *p*-bromoaniline, and the separation after hydrolysis of the reaction products, resulted in the production of pale yellow, crystalline substances (impure), melting at about 110° and 121° respectively, which were not the expected halogenated aminobenzophenones, and at his suggestion the present author has made a further investigation of the reaction. It may be mentioned here that the pale yellow substances referred to have now been found to be the benzoyl derivatives of the halogenated aminobenzophenones, and therefore the normal transformation products, but that owing to the great difficulty with which they are hydrolysed, the usual process for separating the products of the transformation, namely, hydrolysis with alcoholic hydrogen chloride, was insufficiently prolonged for the production of the halogenated aminobenzophenone. The author has hydrolysed these substances, and prepared the corresponding halogenated aminobenzophenones. The results of the investigation show that with chlorine or bromine in the para-position with respect to the original diacylated amino-group one of the benzoyl groups migrates to the ortho-position (with respect to the nitrogen), and the transformation therefore follows the usual course.

EXPERIMENTAL.

*Transformation of Dibenzoyl-*p*-chloroaniline into 5-Chloro-o-benzoylaminobenzophenone, and Hydrolysis of the latter to 5-Chloro-o-aminobenzophenone,*



The method employed consisted in heating *p*-chloroaniline (24 grams) with the quantity of benzoyl chloride requisite to form the dibenzoyl derivative (55 grams), together with zinc chloride (8 grams), in a small flask (fitted with a cork and vertical air condenser terminating in a calcium chloride tube) on an oil-bath, first for two hours at 100—180°, and then for twenty-two to twenty-three hours at 200—220°. The resulting brownish-yellow, resinous cake was powdered, and hydrolysed by prolonged boiling on the water-bath (for twenty-three hours) with 400 c.c. of alcohol and 200 c.c. of concentrated hydrochloric acid. If this hydrolysis is continued only for fourteen hours, as in the earlier experiments, the chief product of the subsequent separation is the non-hydrolysed 5-chloro-*o*-benzoylaminobenzophenone. The resulting brown liquid was distilled in a current of steam, alcohol and ethyl benzoate passing over, and the distillation stopped when a few tarry drops passed over. The liquid was then rendered alkaline, and again distilled in a current of steam, when the unchanged *p*-chloroaniline passed over. When this appeared to have ceased and the distillate became yellow through the presence of a little of the aminochloroketone, the distillation was stopped. After cooling, the brown solid cake, which contained the aminochloroketone, was repeatedly extracted with somewhat dilute hydrochloric or sulphuric acid. The aminochloroketone is a weak base, and as its salts are completely hydrolysed by excess of water, the crude base was thus obtained on diluting the filtrate from the acid extraction. Finally, the tarry residue was heated with concentrated hydrochloric acid and a little alcohol, filtered, and the filtrate similarly treated with water. Any residue consists, besides tarry matter, of a little of the non-hydrolysed benzoylaminochloroketone, but if the original hydrolysis has been sufficiently prolonged this is a mere trace.

Rather less than half of the *p*-chloroaniline employed was recovered, whilst the crude base amounted to about 46 per cent. of the theoretical amount obtainable from the *p*-chloroaniline actually changed. The crude base was purified by dissolving it in hot dilute acid, filtering, diluting with water, and finally recrystallising the base thus separated, either from dilute alcohol or from a mixture of chloroform and light petroleum.

5-*Chloro*-o-*benzoylaminobenzophenone*,

$$C_6H_5{\cdot}CO{\cdot}C_6H_3Cl{\cdot}NH{\cdot}CO{\cdot}C_6H_5,$$

is obtained as the chief product in the above process, if the initial hydrolysis is not sufficiently prolonged, on dissolving the solid residue obtained after the final steam distillation in alcohol, concentrating, and adding dilute sulphuric acid; brownish-yellow crystals separate, which can be purified by dissolving in hot alcohol, digesting with animal charcoal, and recrystallising. It may also be obtained by benzoylating the free aminochloroketone by the Schotten-Baumann method. When prepared in either way it is a pale yellow, very stable, indifferent substance, which separates from alcohol in radiating clusters of silky, needle crystals, melting at 108°. It is very readily soluble in alcohol, benzene, acetic acid, or chloroform. It is hydrolysed only with difficulty. Heating with fairly concentrated sulphuric acid was eventually found to be the most rapid method of effecting the hydrolysis:

0·3238 gave 0·1388 AgCl. Cl = 10·61.

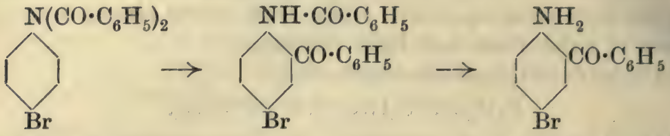
$C_{20}H_{14}O_2NCl$ requires Cl = 10·56 per cent.

5-Chloro-*o*-aminobenzophenone, $C_6H_5{\cdot}CO{\cdot}C_6H_3Cl{\cdot}NH_2$, obtained as above by the hydrolysis of its benzoyl derivative, has previously been prepared (but not analysed) by the hydrolysis of 5-chloro-*o*-acetylaminobenzophenone, obtained by the transformation of acetyl-*o*-chloroaminobenzophenone (Chattaway, Trans., 1904, **85**, 344). It is a weak base, which readily forms salts when dissolved in hot dilute acids, but these salts are very readily hydrolysed by water; the hydrochloride turns yellow in moist air, owing to this hydrolysis. The free base possesses the characteristic properties of orthoaminobenzophenones, namely, intense bright yellow colour and volatility in steam, although steam distillation is so slow that it is impracticable for purposes of purification. Specimens prepared by both methods were found to be identical. It crystallises from alcohol in slender needles melting at 98°:

0·2010 gave 0·1248 AgCl. Cl = 15·36.

$C_{13}H_{10}ONCl$ requires Cl = 15·31 per cent.

*Transformation of Dibenzoyl-*p*-bromoaniline into 5-Bromo-o-benzoylaminobenzophenone, and Hydrolysis of the latter to 5-Bromo-o-aminobenzophenone,*



17·5 Grams of *p*-bromoaniline, 4 grams of zinc chloride, and 30 grams of benzoyl chloride were heated similarly for two hours at 100—180° and twenty-two hours at 200—230°, and the product was hydrolysed by heating with 300 c.c. of alcohol and 200 c.c. of concentrated hydrochloric acid on the water-bath for thirty-seven hours. The aminobromoketone was isolated exactly as in the case of the chloro-compound. The yield of crude base was about 7 grams, and 7 grams of *p*-bromoaniline were recovered, giving a yield of about 41 per cent. of the theoretical. A less tedious separation was effected by treating the powdered product in three separate portions with 200 c.c. each of dilute sulphuric acid (equal volumes of concentrated acid and water), and heating for half or three-quarters of an hour. After cooling, the tarry solid mass was removed, and the filtrate rendered alkaline with potassium or sodium hydroxides. The precipitated aminobromoketone was separated, heated with dilute sulphuric acid, the solution filtered, and the dissolved salt hydrolysed by excess of water; the precipitated base was recrystallised from dilute alcohol. The tarry solid consists chiefly of non-hydrolysed benzoylaminobromobenzophenone, which is separated by dissolving in hot alcohol, adding dilute sulphuric acid, and allowing the solution to cool, when crystals are obtained which are readily purified by recrystallisation (after decolorising with animal charcoal) from alcohol. By this method about two-thirds of the product is obtained as the benzoyl derivative instead of the free base.

5-*Bromo-o-benzoylaminobenzophenone*,

$$C_6H_5\cdot CO\cdot C_6H_3Br\cdot NH\cdot CO\cdot C_6H_5,$$

obtained by this method or by the Schotten-Baumann reaction from the aminobromoketone, closely resembles the corresponding chloro-compound in all respects. It separates from alcohol in pale yellow, silky needles, melting at 122°:

0·1894 gave 0·0935 AgBr. Br = 21·00.

$C_{20}H_{14}O_2NBr$ requires Br = 21·03 per cent.

5-*Bromo-o-aminobenzophenone*, $C_6H_5\cdot CO\cdot C_6H_3Br\cdot NH_2$, also resembles the corresponding chloro-compound very closely. It is a weak base, forming colourless, crystalline salts when dissolved in hot hydrochloric or sulphuric acids (not too dilute).

The salts are extremely easily hydrolysed by water, and turn yellow in moist air for this reason. The hydrochloride appears to be less stable than that of the chloro-compound, but both form platinichlorides. The free base possesses the characteristic intense yellow colour of the *o*-aminobenzophenones, and is somewhat volatile in steam. It is readily soluble in alcohol, chloroform, benzene, etc., and is best crystallised either from dilute alcohol or from a mixture of chloroform and light petroleum, when it separates in radiating masses of needles melting at 111°:

0·1982 gave 0·1352 AgBr. Br = 29·02.

$C_{13}H_{10}ONBr$ requires Br = 28·95 per cent.

The author wishes to acknowledge his indebtedness to Dr. Chattaway, and also to Dr. Baker, in whose laboratory the work has been carried out.

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LX.—*Asymmetric Quinquevalent Nitrogen Compounds of Simple Molecular Constitution.*

By WILLIAM JACKSON POPE and JOHN READ.

TWENTY years ago Le Bel described the preparation of methylethylpropyl*iso*butylammonium salts (*Compt. rend.*, 1891, **112**, 724), together with the mode in which, by allowing a "microbe" to grow in the aqueous solution of the chloride of the above base, he was able to obtain a solution exhibiting a rotatory power of −30′ and −25′; the acetate of the quaternary ammonium base obtained from the solution modified by the organism was also optically active, but the optical activity was so fugitive that it disappeared on converting the salt into the sulphate by means of silver sulphate. As a result of these observations, Le Bel concluded that he had for the first time obtained proof that an asymmetric quaternary ammonium salt could exist in optically active modifications.

The scanty nature of the experimental details given contrasted strongly with the importance of the conclusion deduced, and several workers repeated Le Bel's work without, however, obtaining the positive results which he described. Marckwald in particular (*Ber.*, 1899, **32**, 560) carefully studied the preparation of methylethylpropyl*iso*butylammonium iodide, and devised a method for preparing methylethyl*iso*butylamine, and converting it into the corresponding mixed quaternary ammonium iodide by treatment with propyl iodide; the product was beautifully crystalline, and as it gave a definite, crystalline platinichloride and aurichloride, was obviously a pure single substance. All attempts made by Marckwald and v. Droste-Huelshoff, with the aid of experienced bacteriologists, to render the solution of the corresponding chloride optically active by the method described by Le Bel were fruitless.

Le Bel replied to the paper quoted above, confirming his previous results (*Compt. rend.*, 1899, **129**, 548), giving a few more details as to the preparation and treatment, and stating that he adds a little Liebig's extract to the chloride, and inoculates the solution strongly with *Penicillium glaucum;* as before, however, he described no crystalline products, and quoted no analytical results. He attributed the failure of Marckwald's experiments to the fact that the latter prepared the quaternary ammonium iodide by the action of propyl iodide on methylethyl*iso*butylamine, and suggested that the substance obtained in this way is different from that obtained by the action of methyl iodide on ethylpropyl*iso*butylamine; he further stated that in the combination of methyl iodide with ethylpropyl*iso*butylamine two isomeric products result, one of which, the α-compound, is rendered optically active by the organism, whilst the second, the β-isomeride, is toxic to the organism.

Marckwald then commenced the repetition of the work in accordance with the new particulars given by Le Bel concerning the order in which the four alkyl groups should be introduced, using the same precaution which he had previously adopted, namely, that of isolating in a state of purity each material constituting one stage in the process (*Ber.*, 1899, **32**, 3508). At this juncture, however, Pope and Peachey described the resolution of phenylbenzylmethylallylammonium iodide into its optically active components (Trans., 1899, **75**, 1727). As this case definitely proved that optical activity could be associated with the presence of an asymmetric quinquevalent nitrogen atom, and was followed by others worked out in a similar manner by H. O. Jones and Wedekind, Marckwald did not see fit to expend further time and effort on the confirmation or refutation of Le Bel's previous ambiguous results.

It is now known, however, that unexpected difficulties arise in connexion with the resolution of externally compensated compounds of simple molecular constitution which contain an asymmetric carbon atom (Pope and Read, Trans., 1908, **93**, 794; Perkin and Pope, Trans., 1911, **99**, 1510), and that such substances do not prove easily resolvable into optically active components. The repetition of Le Bel's work is thus of importance in connexion with the question as to whether similar difficulties are to be encountered in the resolution of externally compensated substances of simple molecular constitution which contain an asymmetric nitrogen atom; we have in consequence continued Marckwald's work from the point at which he left it.

p-*Toluenesulphonyl*iso*butylamide*, $C_6H_4Me{\cdot}SO_2{\cdot}NH{\cdot}CH_2{\cdot}CHMe_2$.

p-Toluenesulphonyl chloride (200 grams), contained in a stoppered bottle, is covered with water, and *iso*butylamine (73 grams) cautiously added; the mixture becomes warm, and completely liquefies. Sodium hydroxide solution (420 grams of 10 per cent. solution) is then added in two portions with continued agitation; after mechanically shaking for half an hour, the reaction is complete. The oily product obtained after washing with water remains liquid, in spite of strong cooling and treatment with various solvents; but on boiling a small portion for a short time with sodium hydroxide solution, and cooling, a separation of sodium *p*-toluenesulphonate is obtained, and the residual oily material slowly crystallises. The crystalline substance thus obtained, when used for the inoculation of the main bulk of oil, causes rapid crystallisation to occur, and it is to be presumed that the difficulty with which crystallisation takes place in the first instance is due to contamination with *p*-toluenesulphonyl chloride, which is hydrolysed by boiling with sodium hydroxide. After breaking up the crystalline cake, washing with water, and crystallising from light petroleum, the substance is obtained in a 98 per cent. yield as colourless, hard, glistening prisms, melting at 74—75°:

0·1056 gave 0·2245 CO_2 and 0·0724 H_2O. C=57·98; H=7·69.

$C_{11}H_{17}O_2NS$ requires C=58·09; H=7·54 per cent.

On treatment with concentrated sodium hydroxide solution, *p*-toluenesulphonyl*iso*butylamide yields a crystalline *sodio*-derivative, which is immediately hydrolysed on addition of water.

p-*Toluenesulphonylpropyl*iso*butylamide*,
$C_6H_4Me{\cdot}SO_2{\cdot}N(CH_2{\cdot}CH_2{\cdot}CH_3)CH_2{\cdot}CHMe_2$.

This substance was prepared by Marckwald (*Ber.*, 1899, **32**, 3509) by heating *p*-toluenesulphonylpropylamide with the equivalent quantities of alcoholic alkali and *iso*butyl bromide at 100°. We prepare it more conveniently by mixing *p*-toluenesulphonyl*iso*butylamide (200 grams) with powdered potassium hydroxide (20 grams), sufficient alcohol to form a stiff paste, and propyl bromide (5 per cent. excess), and heating the mass under a reflux condenser in an oil-bath at 120—125° for five hours; after distilling off the alcohol at 125°, cooling, and washing with water, the oil is extracted with ether, washed, and dried over calcium chloride. After evaporation of the ether, crystallisation may be caused by inoculation with solid material obtained by boiling with sodium hydroxide as before described; the product is crystallised from light petroleum or warm alcohol containing a little water. The purified substance melts at 54·5°, instead of at 59—60° as stated by Marckwald; a yield of about 70 per cent. is obtained, and this may be increased by again treating the oily products from the mother liquors with propyl bromide and potassium hydroxide.

*Propyl*iso*butylamine*, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CH_2{\cdot}CHMe_2$.

This base was prepared by Marckwald (*loc. cit.*) by hydrolysing its *p*-toluenesulphonyl derivative with chlorosulphonic acid, as suggested by Hinsberg (*Annalen*, 1891, **265**, 178) in connexion with the preparation of other secondary amines; we were unable to cause the hydrolysis to proceed very satisfactorily. *p*-Toluenesulphonylpropyl*iso*butylamide (140 grams) was slowly heated with chlorosulphonic acid (75 grams) to 130—150°, and maintained at that temperature for two to three hours; after cooling, pouring into water, and adding excess of alkali, the product was distilled in a current of steam, and the distillate evaporated to dryness after acidification with hydrochloric acid. The hydrochloride obtained from a large quantity (710 grams) of *p*-toluenesulphonylpropyl*iso*butylamide on distillation with very concentrated potassium hydroxide gave a good yield of base (145 grams), which proved to be a complex mixture, and which, when distilled through a Young fractionating column, yielded fractions boiling at 55—60° (20 grams), 60—70° (17 grams), 75—100° (11 grams), 100—120° (4 grams), and 122—124° (90 grams). The fraction boiling at 55—60° was found, by conversion into its *p*-toluenesulphonyl derivative, to consist largely of propylamine, and to contain some *iso*butylamine and propyl*iso*butylamine, so that the base obtained by the treatment with chlorosulphonic acid presumably consisted of a mixture of the two primary and the one secondary amine. The various fractions were therefore dissolved in about twice the calculated quantity of hydrochloric acid (10 per cent.), twice the calculated quantity of sodium nitrite added to the ice-cold solution, and the liquid warmed for some time on the water-bath; the nitrosoamine produced was separated with the aid of ether, and, after evaporation of the latter solvent, hydrolysed by heating at 110° with hydrochloric acid, a constant stream of hydrogen chloride being passed through the mass during the process (Ladenburg, *Ber.*, 1879, **12**, 949). After evaporating to dryness, the pure secondary base was isolated by distillation with concentrated potassium hydroxide and subsequent fractional distillation as a colourless oil boiling at 122—124°.

It is thus evident that the hydrolysis of the acidic derivative of the secondary base by the Hinsberg method yields the two possible primary bases, in addition to the required propyl*iso*butylamine.

*Ethylpropyl*iso*butylamine*, $CH_3{\cdot}CH_2{\cdot}N(CH_2{\cdot}CH_2Me)CH_2{\cdot}CHMe_2$.

Propyl*iso*butylamine, boiling at 122—124° (40 grams), was heated with the calculated amount of ethyl iodide (55 grams) and a slight excess of alcoholic potassium hydroxide for six hours on the water-bath; separation of potassium iodide and evolution of heat were observed on adding the iodide. The tertiary base was isolated by evaporation to dryness with hydrochloric acid, and distillation of the residue with concentrated potassium hydroxide; secondary base was eliminated from the product as nitrosoamine, and the tertiary base thus purified (37 grams) boiled at 142—147°. With platinic chloride in hydrochloric acid solution it yields a *platinichloride*, which is readily soluble in water; this, on crystallisation from hot alcohol, is obtained in fine, orange-coloured needles, melting and decomposing at 204—207°:

0·5983 gave 0·1694 Pt. Pt = 28·32.

$(C_9H_{21}N)_2,H_2PtCl_6$ requires Pt = 28·05 per cent.

*Methylethylpropyl*iso*butylammonium Iodide*,
$CH_3{\cdot}N(C_2H_5)(C_3H_7)(C_4H_9)I$.

On mixing ethylpropyl*iso*butylamine with a slight excess of methyl iodide, the liquid soon becomes turbid, and deposits a yellow oil, which gradually changes to a white, crystalline mass; after two or three hours the whole product is solid, and is then left in a vacuum desiccator. The product is very soluble in water, chloroform, or alcohol, but insoluble in ether, and is precipitated from the alcoholic solution as an oil on addition of ether. It is conveniently purified by crystallisation from anhydrous acetone, the separated material being washed with acetone containing a little anhydrous ether; the yield is theoretical:

0·2096 reacted with 7·3 c.c. $N/10$-$AgNO_3$. I = 44·20.

$C_{10}H_{24}NI$ requires I = 44·52 per cent.

The salt melts at 195°, and the corresponding *platinichloride*, which is easily soluble in water and less so in alcohol, crystallises from the latter solvent in small, yellow crystals, melting at 241° with profound decomposition:

0·4068 gave 0·1108 Pt. Pt=27·24.

$(C_{10}H_{24}N)_2PtCl_6$ requires Pt=26·97 per cent.

The *aurichloride* is practically insoluble in cold water, and crystallises from warm alcohol in very characteristic, lustrous, yellow scales, melting at 101°:

0·3056 gave 0·1216 Au. Au=39·79.

$C_{10}H_{24}N,AuCl_4$ requires Au=39·66 per cent.

The quaternary ammonium iodide which Marckwald obtained by the action of propyl iodide on methylethyl*iso*butylamine melted at 196·5°, the corresponding platinichloride melted and decomposed at 236°, and the aurichloride at 103°; the description of his salts which Marckwald gives (*Ber.*, 1899, **32**, 563) corresponds closely with ours, and there is thus no doubt that the same quaternary ammonium iodide is obtained by the action of methyl iodide on ethylpropyl*iso*butylamine as by the action of propyl iodide on methylethyl*iso*butylamine.

We therefore conclude that Le Bel's contention (*Compt. rend.*, 1899, **129**, 548) that Marckwald's quaternary ammonium compound differed from his because of the different order in which the alkyl groups were introduced, is erroneous.

It is now instructive to contrast the method of preparation of Le Bel's methylethylpropyl*iso*butylammonium iodide with those devised by Marckwald and ourselves. The following is an abbreviated statement of the method described by Le Bel for the preparation of this substance (*loc. cit.*). He treats commercial *iso*butylamine, prepared from fermentation alcohol, with half an equivalent of propyl iodide; the volatile bases, dried with potassium hydroxide, are fractionated, and propyl*iso*butylamine, boiling at 125°, is easily isolated. The latter, similarly treated with ethyl iodide, yields the triamine, which boils at 146° and must be carefully fractionated; this compound is then treated with a large excess of methyl iodide. The latter interaction is violent, and is applied to 25 grams at a time of the triamine contained in a retort; the material projected from the retort is collected, and again treated with methyl iodide, and ultimately the whole is heated to 120°.

In order to obtain some measure of the violence with which ethylpropyl*iso*butylamine reacts with methyl iodide, the former substance (8 grams) was mixed at 15° with methyl iodide (11 grams) at 14·5°. The temperature of the mixture immediately fell to 12°, and after ten minutes rose again to 15°, and after twenty minutes, when reaction was practically at an end, rose further to 24°, which was the maximum temperature attained. The difference in the behaviour towards methyl iodide of the tertiary base, as described by Le Bel and ourselves, is so great as to indicate that the two supposed tertiary bases were not identical. As the composition of our ethylpropyl*iso*butylamine was checked by analysis at each stage during its preparation, and as Le Bel quotes no analysis in support of his more imperfect method of preparation, it is indicated that Le Bel's product was not ethylpropyl*iso*butylamine.

We therefore conclude that Le Bel did not obtain methylethylpropyl*iso*butylammonium iodide; moreover, as this is the only substance containing an asymmetric quinquevalent nitrogen atom that could possibly have been formed by the series of interactions which he described, the slight optical activity he observed after submitting the product to the action of the micro-organism cannot be associated with the presence of an asymmetric nitrogen atom. The observed optical activity is rather to be ascribed to some impurity introduced with, or formed by, the organism.

*Attempts to Resolve Methylethylpropyl*iso*butylammonium Iodide into Optically Active Components.*

Since Marckwald and v. Droste-Huelshoff (*Ber.*, 1899, **32**, 563) made many unsuccessful attempts to obtain optical activity by the action of micro-organisms on methylethylpropyl*iso*butylammonium chloride, we have not further studied this particular method of resolution, but have investigated the salts of the base with optically active acids.

*Methylethylpropyl*iso*butylammonium* d-*β-Camphorsulphonate,* $(CH_3)(C_2H_5)(C_3H_7)(C_4H_9)N\cdot SO_3\cdot C_{10}H_{15}O$.

Methylethylpropyl*iso*butylammonium iodide in alcoholic solution is heated with the corresponding quantity of silver *d*-*β*-camphorsulphonate on the water-bath until reaction is complete; after filtration and subsequent evaporation, a white, crystalline salt results, which is not deliquescent. The salt was subjected to prolonged fractional crystallisation, first from benzene, in which it is sparingly soluble, and later from ethyl acetate containing a little alcohol; the various fractions are thus obtained in small, colourless, iridescent needles, melting at 224—225°, and appear to consist of but one substance:

0·1096 gave 0·2472 CO_2 and 0·1018 H_2O. C = 61·51; H = 10·39.

$C_{20}H_{39}O_4NS$ requires C = 61·64; H = 10·10 per cent.

The first and last fractions gave the following results on determination of the rotatory powers, the weight taken being made up to 30 c.c. with water, and the solutions examined in mercury green light at 17° in a 4-dcm. tube.

First fraction: 0·3756 gram gave α +0·82°, $[\alpha]$ +16·4°, $[M]$ +63·8°.

Last fraction: 0·2157 gram gave α +0·47°, $[\alpha]$ +16·3°, $[M]$ +63·4°.

Ammonium *d-β*-camphorsulphonate gives [M] for Hg_{green} +66·6° in aqueous solution, and it is clear that no resolution of the asymmetric nitrogen compound has been effected (Trans., 1910, **97**, 2213).

*Methylethylpropyl*iso*butylammonium* d-*α-Bromocamphor-π-sulphonate*, $(CH_3)(C_2H_5)(C_3H_7)(C_4H_9)N\cdot SO_3\cdot C_{10}H_{14}OBr$.

This salt is prepared in a similar manner to the foregoing, and is obtained on evaporation of the solvent as a white, crystalline, deliquescent mass. It dissolves freely in acetone, benzene, or chloroform, and crystallises readily on cooling its solution in hot anhydrous ethyl acetate solution; after prolonged fractional crystallisation from this solvent a number of fractions melting at 182° were obtained:

0·1088 gave 0·2046 CO_2 and 0·0827 H_2O. C=51·29; H=8·51.

$C_{20}H_{38}O_4NBrS$ requires C=51·25; H=8·18 per cent.

The first and last fractions gave the following results on polarimetric examination, the weight taken being made up to 30 c.c. with water, and the solution examined in a 4-dcm. tube at 17°:

First fraction :		$Hg_{green.}$	$Hg_{yellow.}$	$Na_{yellow.}$
0·1899 gram	α	+ 1·86°	+ 1·59°	+ 1·50°
	$[\alpha]$ ...	+ 73·5	+ 62·8	+ 59·2
	$[M]$ ...	+344	+294	+277

Hg_{green}/Na_{yellow}=1·242 ; Hg_{yellow}/Na_{yellow}=1·061.

Last fraction :				
0·2129 gram	α	+ 2·07°	+ 1·77°	+ 1·67°
	$[\alpha]$ ...	+ 72·9	+ 62·3	+ 58·8
	$[M]$ ...	+341	+292	+275

Hg_{green}/Na_{yellow}=1·240 ; Hg_{yellow}/Na_{yellow}=1·060.

As the corresponding values for the rotatory dispersions of the ammonium salt of the acid are Hg_{green}/Na_{yellow}=1·243 and Hg_{yellow}/Na_{yellow}=1·059 (Trans., 1910, **97**, 2201), it is obvious that again no resolution has been effected.

*Stability of Methylethylpropyl*iso*butylammonium Salts towards Water.*

As the treatment to which Le Bel subjected his quaternary ammonium salt appears somewhat drastic and likely to lead to its decomposition, 3 grams of the iodide were treated in the manner which he describes for the preparation of the chloride. The pure iodide was heated in aqueous solution on the water-bath with excess of lead chloride, the solution cooled and filtered, and the treatment with lead chloride repeated; the filtrate was then warmed with silver chloride, filtered, and treated with hydrogen sulphide. After filtration, the solution was repeatedly evaporated on the water-bath with addition of water to remove hydrochloric acid; the chloride was thus obtained as a deliquescent syrup. The precipitates of lead and silver salts from which the organic chloride had been filtered were in turn warmed with dilute hydrochloric acid, and treated exhaustively with hydrogen sulphide; the solution was filtered, boiled to remove hydrogen sulphide, and treated with silver chloride to remove iodide. The two solutions of chloride thus obtained were precipitated with auric chloride, and the crystalline aurichloride weighed; the quantities obtained corresponded with 2·60 grams of quaternary iodide in the case of the chloride solution, and 0·36 gram in that of the extract. The quantity of aurichloride recovered thus corresponded with 2·96 grams of iodide, instead of 3 grams as was originally treated; the aurichloride melted at 101°. It thus appears that the asymmetric quaternary nitrogen radicle is possessed of very great stability towards water and acids.

Action of Methyl Iodide on Tertiary Amines.

Pope and Harvey found (Trans., 1901, **79**, 833) that phenylbenzylmethylallylammonium iodide is most conveniently prepared by the action of the tertiary base on methyl iodide in alcoholic solution; we therefore attempted to prepare methylethylpropyl*iso*butylammonium iodide by mixing ethylpropyl*iso*butylamine with methyl iodide in ethereal solution. The base (10 grams) was dissolved in dry ether (30 grams), and methyl iodide (13 grams) added gradually. The solution immediately became turbid, and a white, crystalline salt slowly separated without appreciable rise of temperature; after two days the crystalline material (8 grams) was separated, and the filtrate mixed with a further quantity of methyl iodide, which led to the deposition of more quaternary iodide (8·5 grams) on keeping for some days.

The salt thus obtained is very soluble in water, alcohol, or chloroform, but insoluble in absolute ether; it was purified by inducing its crystallisation by gradual addition of absolute ether to its alcoholic solution, and was thus obtained in colourless, crystalline needles, melting and decomposing at about 170°. Analysis showed, however, that the salt thus obtained was not the expected methylethylpropyl*iso*butylammonium iodide, but *dimethylpropyl*iso*butylammonium iodide*:

0·2367 gram required 8·75 c.c. *N*/10-$AgNO_3$. I=46·9.

$C_9H_{22}NI$ requires I=46·8 per cent.
($C_{10}H_{24}NI$ „ I=44·5 per cent.)

The *platinichloride* crystallises from hot alcohol in minute, orange scales, and is sparingly soluble in boiling water or alcohol:

0·5024 gave 0·1421 Pt. Pt=28·28.

$(C_9H_{22}N)_2PtCl_6$ requires Pt=28·05 per cent.
[$(C_{10}H_{24}N)_2PtCl_6$ „ Pt=26·97 „ „]

During the action of methyl iodide on ethylpropyl*iso*butylamine in ethereal solution it thus appears that the ethyl group becomes displaced from the tertiary amine by a methyl radicle, whilst it has been shown above that no such replacement occurs when the amine and the alkyl iodide are brought together in absence of a solvent. It consequently appeared desirable to investigate the action of methyl iodide on other tertiary amines of similar molecular weight in presence and absence of ether.

On treating tripropylamine with methyl iodide, with and without the addition of several volumes of dry ether as a solvent, combination occurred rapidly, and a white, crystalline substance separated; this in both cases was identified by analysis and physical properties as the methyltripropylammonium iodide of Wedekind (*Ber.*, 1902, **35**, 776). Similarly, on treating triethylamine with an equivalent proportion of methyl iodide in presence and absence of ether as a solvent, the same white product was obtained in each case, and was found to be *methyltriethylammonium iodide*. The substance crystallises from a mixture of ether and alcohol in transparent needles melting at above 230°:

0·1473 precipitated 7·15 c.c. *N*/10-$AgNO_3$. I=52·6.

$C_7H_{18}NI$ requires I=52·2 per cent.
($C_6H_{16}NI$ „ I=55·4 „ „)

The same product is obtained when a large excess of methyl iodide is added to the tertiary amine in ethereal solution. The corresponding *platinichloride* crystallises from hot water in small, orange, granular crystals, melting at above 220°:

0·2798 gave 0·0855 Pt. Pt=30·59.

$(C_7H_{18}N)_2PtCl_6$ requires Pt=30·47 per cent.
[$(C_6H_{16}N)_2PtCl_6$ „ Pt=31·86 „ „]

It is thus proved that whilst triethylamine and tripropylamine merely form additive products with methyl iodide in ethereal solution, the mixed tertiary base, ethylpropyl*iso*butylamine, behaves abnormally, and allows its ethyl group to become displaced by methyl when treated with methyl iodide in ethereal solution.

The reason for the abnormal behaviour of the mixed tertiary amine is no doubt connected with the observation of Pope and Harvey (Trans., 1901, **79**, 831) that *d*- or *l*-phenylbenzylmethylallylammonium iodide rapidly undergoes optical inversion on preservation in chloroform solution. The latter observation was attributed by these authors to the occurrence of dissociation, in accordance with the equation:

$$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)NI \rightleftarrows (CH_3)(C_3H_5)(C_6H_5)N + C_7H_7I,$$

and after prolonged investigation the explanation thus provided has been proved to be correct by Wedekind (*Ber.*, 1902, **35**, 766). It may therefore be suggested that in an appropriate solvent, methylethylpropyl*iso*butylammonium iodide dissociates into the four tertiary amines of which the formation is possible, namely, methylpropyl*iso*butylamine, methylethylpropylamine, methylethyl*iso*butylamine, ethylpropyl*iso*butylamine, and the corresponding alkyl iodides, but that dissociation into methylpropyl*iso*butylamine and ethyl iodide proceeds to a far greater extent than any one of the other possible changes. Then, as soon as methylpropyl*iso*butylamine is thus formed, it combines with the methyl iodide present to yield dimethylpropyl*iso*butylammonium iodide, which at once crystallises, being insoluble in ether; the removal of the latter compound from the solution as rapidly as it is formed prevents the separation of any other quaternary ammonium iodide from the solution.

Other cases of replacement of alkyl groups closely connected with the above have been described by H. O. Jones (Trans., 1903, **83**, 1408; 1905, **87**, 1721) and by Wedekind (*Ber.*, 1905, **38**, 438).

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LXI.—*The Synthesis of Glyoxaline Derivatives Allied to Pilocarpine.*

By Frank Lee Pyman.

The idea of preparing glyoxalines containing acidic groups analogous to the homopilopic complex in pilocarpine by condensing a suitable bromoglyoxaline with substances such as ethyl sodiomalonate was put forward by Jowett in 1905 (Trans., **87**, 405). Owing, however, to the difficulty of obtaining at the time suitable bromoglyoxalines in good yield, no condensation experiments were actually carried out. Since then the present author—continuing this line of work at Dr. Jowett's request—has prepared and characterised the bromo- and dibromo-derivatives of 4(or 5)-methylglyoxaline, 1:4-dimethylglyoxaline, and 1:5-dimethylglyoxaline (Trans., 1910, **97**, 1814). A number of bromoglyoxalines being thus available, attempts were made to bring them into reaction in various ways, but in every case unsuccessfully.

In the first place, it was found that these compounds were quite unaffected when heated with ethyl sodiomalonate or ethyl sodioacetoacetate under various conditions, for in each case the bromoglyoxaline was recovered unchanged, and no bromide could be detected in the reaction mixture by means of silver nitrate.

The stability of the bromoglyoxalines indicated by these results is comparable with that of bromobenzene. This compound may be readily brought into reaction by Grignard's method, and attempts were therefore made to convert bromoglyoxalines into magnesium glyoxalyl bromides, which might then be used for the preparation of derivatives in the usual manner.

All attempts, however, to effect the combination of bromoglyoxalines with magnesium, whether by adding traces of iodine or methyl iodide or by using "active" magnesium (Baeyer, *Ber.*, 1905, **38**, 2759), were unsuccessful.

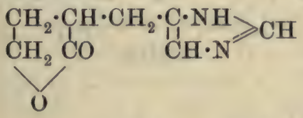
Finally, it was thought that bromoglyoxalines might possibly be brought into reaction by heating them with magnesium alkyl halides at high temperatures, a method employed by Grignard (*Compt. rend.*, 1904, **138**, 1048), and subsequently by Wohl and Berthold (*Ber.*, 1910, **43**, 2177), for the preparation of derivatives of ω-bromophenetole. This method was also unsuccessful, for on heating 2:4-dibromo-1:5-dimethylglyoxaline with magnesium methyl iodide or magnesium phenyl bromide for several hours in boiling xylene, the bromine atoms were to some extent replaced, not by alkyl groups, but by hydrogen, 2(or 4)-bromo-1:5-dimethylglyoxaline and

1:5-dimethylglyoxaline being formed. In consequence of these results, attempts to utilise bromoglyoxalines for synthetic purposes were abandoned.

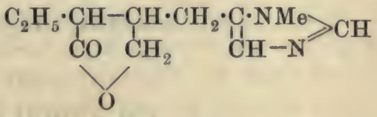
Later, however, the method of preparing glyoxaline derivatives recently employed in the synthesis of 4(or 5)-β-aminoethylglyoxaline (Trans., 1911, **99**, 668) and of histidine (Trans., 1911, **99**, 1386) were applied to the preparation of a number of new compounds, from which a possible physiological action was expected.

The physiological examination of these compounds was carried out by Dr. P. P. Laidlaw, of the Wellcome Physiological Research Laboratories, to whom the author is much indebted, and the results are briefly indicated in the paper.

In the first place, it seemed of interest to prepare the *lactone* of *α(β-hydroxyethyl)β-glyoxaline-*4(or 5)*-propionic acid* (I), for this base has certain constitutional features in common with pilocarpine (II), both compounds containing a glyoxaline ring linked through a methylene group with a butyrolactone residue:

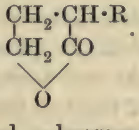


(I.)

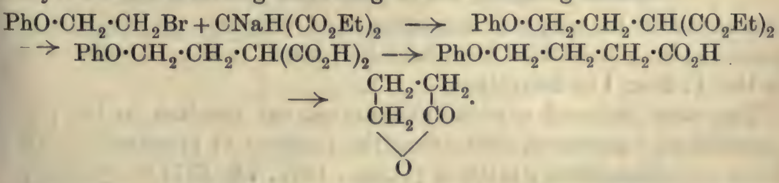


(II.)

This was effected substantially by the method devised by Bentley, Haworth, and Perkin (Trans., 1896, **69**, 169) for the synthesis of lactones of the general formula:



These chemists condensed ω-bromophenetole with ethyl sodiomalonate, hydrolysed the resulting crude ethyl γ-phenoxyethylmalonate, and isolated γ-phenoxyethylmalonic acid; this was converted into γ-phenoxybutyric acid by heating to 200°, and phenol was removed from the latter by means of fuming hydrobromic acid, butyrolactone resulting according to the following scheme:

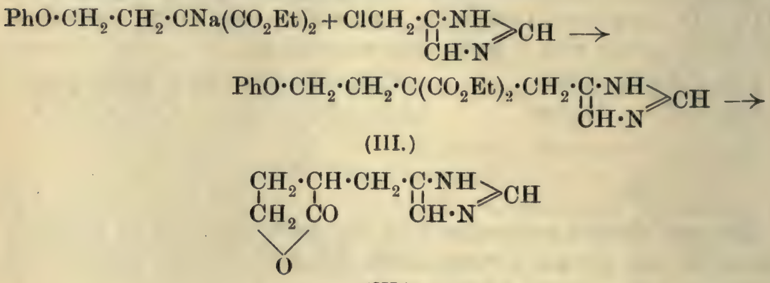


$$PhO\cdot CH_2\cdot CH_2Br + CNaH(CO_2Et)_2 \longrightarrow PhO\cdot CH_2\cdot CH_2\cdot CH(CO_2Et)_2 \longrightarrow PhO\cdot CH_2\cdot CH_2\cdot CH(CO_2H)_2 \longrightarrow PhO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO_2H \longrightarrow$$

By using the sodium derivatives of ethyl alkylmalonates in the first instance, they obtained the corresponding alkylbutyrolactones.

In the present investigation ethyl γ-phenoxyethylmalonate, which was prepared by the above method, was first isolated and purified. Two molecules of its sodium derivative were then condensed with one molecule of 4(or 5)-chloromethylglyoxaline hydrochloride, *ethyl* 4(or 5)-*glyoxalinemethyl*-γ-*phenoxyethylmalonate* (III) being formed. The salts of this base did not crystallise readily, but a small amount of the *hydrogen oxalate* was obtained in a pure state. Fortunately, it is not necessary to purify the reaction product at this stage, for on heating it with concentrated hydrochloric acid at 150° for two hours, it is converted at once into the *lactone* of α(*β-hydroxyethyl*)*β-glyoxaline*-4(or 5)-*propionic acid* (IV). This is readily isolated and purified in the form of its *picrate*, and is obtained in a yield amounting to 38 per cent. of the theoretical, calculated on the 4(or 5)-chloromethylglyoxaline hydrochloride employed.

The reaction may be represented as follows:



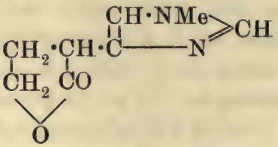
$$\mathrm{PhO{\cdot}CH_2{\cdot}CH_2{\cdot}CNa(CO_2Et)_2 + ClCH_2{\cdot}}\begin{array}{l}\mathrm{C{\cdot}NH}\\ \mathrm{CH{\cdot}N}\end{array}\!\!\gg\!\mathrm{CH} \longrightarrow$$

$$\mathrm{PhO{\cdot}CH_2{\cdot}CH_2{\cdot}C(CO_2Et)_2{\cdot}CH_2{\cdot}}\begin{array}{l}\mathrm{C{\cdot}NH}\\ \mathrm{CH{\cdot}N}\end{array}\!\!\gg\!\mathrm{CH} \longrightarrow$$

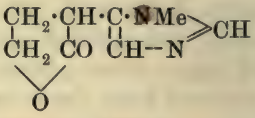
(III.)

(IV.)

On physiological examination, however, this base was found to possess no pilocarpine-like action. A quantity was then methylated with the view of preparing the two isomeric *N*-methyl derivatives (V*a*) and (V*b*), but only one of the two isomerides was isolated from the mixture in a pure condition, and this was physiologically inactive; no experiments have been performed to show whether this is the 1:4- or 1:5-derivative.



and



(V*a*.) (V*b*.)

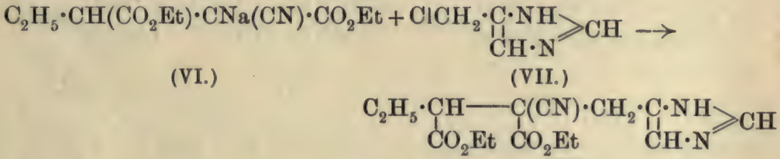
The next series of experiments carried out resulted in the preparation of compounds containing the skeleton of pilocarpine. By Bone and Sprankling's method (Trans., 1899, **75**, 857) of synthesising alkylsuccinic acids, the esters of substituted α-bromo-fatty acids are condensed with ethyl sodiocyanoacetate, yielding ethyl α-cyano-β-ethylsuccinates; these may be again alkylated on the α-carbon atom, yielding ethyl α-cyano-αβ-dialkylsuccinates. Both classes of compounds form oils of constant boiling point, which must be mixtures of the two possible racemic forms, *ddll* and *dlld*, on account of the method of synthesis.

On hydrolysis of the ethyl α-cyano-αβ-dialkylsuccinates by means of concentrated hydrochloric acid, the cyano-group is removed, but the asymmetry of both the carbon atoms is preserved, and a mixture of the *ddll* and *dlld* (so-called *cis* and *trans*) αβ-dialkylsuccinic acids results, which can usually be separated by crystallisation:

$$\mathrm{R{\cdot}CHBr{\cdot}CO_2Et + CHNa(CN){\cdot}CO_2Et} \longrightarrow$$
$$\mathrm{R{\cdot}CH(CO_2Et){\cdot}CH(CN){\cdot}CO_2Et} \xrightarrow{\mathrm{NaOEt+R'I}}$$
$$\mathrm{R{\cdot}CH(CO_2Et){\cdot}CR'(CN){\cdot}CO_2Et} \xrightarrow{\text{conc. HCl}} \mathrm{R{\cdot}CH(CO_2H){\cdot}CHR'{\cdot}CO_2H}$$

Ethyl α-cyano-β-ethylsuccinate formed the starting point of the synthesis mentioned below. This ester was prepared by Jowett (Trans., 1901, **79**, 1348) by the above method as an intermediate product in the synthesis of ethyltricarballylic acid, an oxidation product of the homopilopic acid obtained from pilocarpine.

This ester forms an oil of constant boiling point. When its sodium derivative (VI) is condensed with 4(or 5)-chloromethylglyoxaline hydrochloride (VII), a large quantity of basic ester is formed. This doubtless consists of a mixture of the two isomeric (*ddll* and *dlld*) *ethyl α-cyano-α-*4(or 5)*-glyoxalinemethyl-β-ethylsuccinates* (VIII):



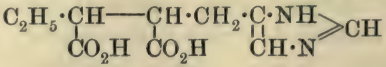
$$\mathrm{C_2H_5{\cdot}CH(CO_2Et){\cdot}CNa(CN){\cdot}CO_2Et + ClCH_2{\cdot}}\begin{array}{l}\mathrm{C{\cdot}NH}\\ \|\\ \mathrm{CH{\cdot}N}\end{array}\!\!>\mathrm{CH} \longrightarrow$$

(VI.) (VII.)

$$\begin{array}{l}\mathrm{C_2H_5{\cdot}CH}\\ \quad\;|\\ \quad\mathrm{CO_2Et}\end{array}\!\!-\!\!\begin{array}{l}\mathrm{C(CN){\cdot}CH_2{\cdot}}\\ |\\ \mathrm{CO_2Et}\end{array}\begin{array}{l}\mathrm{C{\cdot}NH}\\ \|\\ \mathrm{CH{\cdot}N}\end{array}\!\!>\mathrm{CH}$$

(VIII.)

When the crude basic ester is converted into its acid oxalate, and crystallised from water, just half of it can be separated in a crystalline form as a sparingly soluble salt melting at 125—128° (corr.), and the base regenerated from this salt forms well defined crystals melting at 105—106° (corr.). This base obviously represents one of the two isomeric (*ddll* or *dlld*) ethyl α-cyano-α-4(or 5)-glyoxalinemethyl-β-ethylsuccinates in a pure state. The half of the crude basic esters remaining after the separation of the oxalate melting at 125—128° was not obtained crystalline, either as salt or base. It doubtless consists of the isomeric ethyl α-cyano-α-4(or 5)-glyoxalinemethyl-β-ethylsuccinate more or less contaminated with the base melting at 105—106°, for it yields on hydrolysis the same products in the same proportion; thus on hydrolysing either the crystalline (m. p. 105—106°) or oily ester with concentrated hydrochloric acid, apparently the same mixture of the two α-4(or 5)-*glyoxalinemethyl-β-ethylsuccinic acids* (IX) is formed, for in each case the product gradually deposited only a small amount of the same crystalline acid, melting at 236° (corr.), the bulk remaining amorphous. On



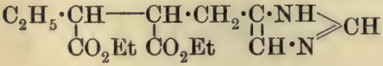
$$\begin{array}{llll} C_2H_5\cdot CH & \!\!-\!\!\!-\, CH\cdot CH_2\cdot & C\cdot NH & \\ & CO_2H \quad CO_2H & CH\cdot N & \!\!\!\gg CH \end{array}$$

(IX.)

the supposition that an equilibrium mixture of the two acids had been obtained, the amorphous acids were on one occasion again subjected to treatment with concentrated hydrochloric acid, but no more of the crystalline acid could be isolated from the product.

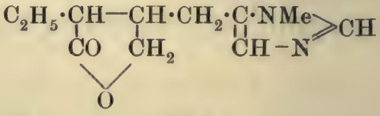
The remaining amorphous acids were then esterified, and an attempt made to separate the resulting ethyl α-4(or 5)-glyoxalinemethyl-β-ethylsuccinates by crystallisation of the hydrogen oxalates, but although crystalline salts were obtained, no satisfactory separation took place.

On esterifying the pure, crystalline α-4(or 5)-glyoxalinemethyl-β-ethylsuccinic acid melting at 236° (corr.) with absolute alcohol and hydrogen chloride, *ethyl* α-4(or 5)-*glyoxalinemethyl-β-ethylsuccinate* (X) was obtained. It was isolated in the form of its beautifully crystalline *hydrogen oxalate*, and in view of the similarity of its structure to that of pilocarpine (XI) was submitted to physiological examination; it proved to be practically inactive:



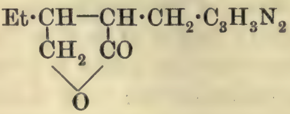
$$\begin{array}{llll} C_2H_5\cdot CH & \!\!-\!\!\!-\, CH\cdot CH_2\cdot & C\cdot NH & \\ & CO_2Et \; CO_2Et & CH\cdot N & \!\!\!\gg CH \end{array}$$

(X.)

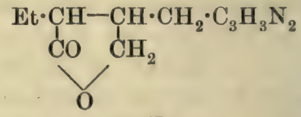


(XI.)

It may perhaps be mentioned at this point that had the isomeric α-4(or 5)-glyoxalinemethyl-β-ethylsuccinic acids been obtainable in good yield, the preparation of their anhydrides, the reduction of these to the corresponding lactones, followed by methylation, and resolution of the products were to have been carried out with the object of synthesising pilocarpine. Owing, however, to the poor yields of the acids, these experiments were discontinued, for each of the (2) corresponding anhydrides might yield two isomeric lactones (A and B) on reduction, and each of the (4) lactones would



(A.)

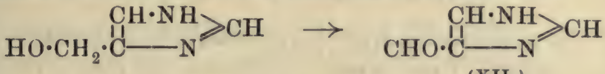


(B.)

yield on methylation two isomeric (1:4- and 1:5-) *N*-methyl derivatives, thus giving rise in all to eight optically inactive (externally compensated) isomerides of pilocarpine, which on resolution would yield sixteen optically active forms. In view, therefore, of the poor yield of the crystalline succinic acid, this synthesis was abandoned.

Since it is known that the benzoic acid esters of many amino-alcohols have valuable local anæsthetic properties, 4(or 5)-*benzoyloxymethylglyoxaline*, $Ph\cdot CO_2\cdot CH_2\cdot C_3H_3N_2$, was next prepared, but this compound proved to be entirely unsuitable for its intended use, since the salts reacted strongly acid in aqueous solution. This compound was readily obtained by heating together 4(or 5)-hydroxymethylglyoxaline and benzoyl chloride; 4(or 5)-p-*nitrobenzoyloxymethylglyoxaline* was similarly prepared.

The preparation of 4(or 5)-*glyoxalineformaldehyde* (XII), a compound which may prove of value in synthetic experiments, is also recorded. This substance was prepared by the oxidation of the corresponding alcohol, 4(or 5)-hydroxymethylglyoxaline:



$$HO\cdot CH_2\cdot\begin{array}{l}CH\cdot NH\\ \|\\ C\text{——}N\end{array}\!\!>CH \longrightarrow CHO\cdot\begin{array}{l}CH\cdot NH\\ \|\\ C\text{——}N\end{array}\!\!>CH$$

(XII.)

In conclusion, the properties of the free base, 4(or 5)-*β-aminoethylglyoxaline*, which has not previously been isolated, and of some new salts of this compound, are described.

EXPERIMENTAL.

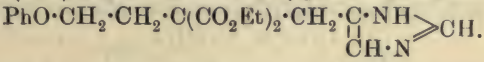
Ethyl γ-Phenoxyethylmalonate, $PhO\cdot CH_2\cdot CH_2\cdot CH(CO_2Et)_2$.

This ester was prepared by the method given by Bentley, Haworth, and Perkin (*loc. cit.*), and fractionated under diminished pressure, when it was obtained as a colourless oil boiling at 226°/40 mm. Although it has previously been purified by Fischer and Blumenthal (*Ber.*, 1907, **40**, 106), and also by Leuchs (*Ber.*, 1911, **44**, 1507), who has recently described an improved method affording an 85 per cent. yield, it does not appear to have been analysed:

0·1304 gave 0·3078 CO_2 and 0·0822 H_2O. C=64·4; H=7·1.

$C_{15}H_{20}O_5$ requires C=64·3; H=7·2 per cent.

Ethyl 4(or 5)-*Glyoxalinemethyl-γ-phenoxyethylmalonate*,



$$PhO\cdot CH_2\cdot CH_2\cdot C(CO_2Et)_2\cdot CH_2\cdot\begin{array}{l}C\cdot NH\\ \|\\ CH\cdot N\end{array}\!\!>CH.$$

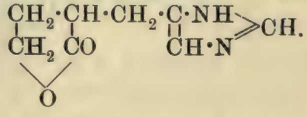
To 2·3 grams of sodium dissolved in 50 c.c. of absolute alcohol, 28 grams of ethyl γ-phenoxyethylmalonate were added, followed by a solution of 7·6 grams of 4(or 5)-chloromethylglyoxaline hydrochloride in 40 c.c. of absolute alcohol. The mixture was boiled for one hour under a reflux condenser, filtered from sodium chloride, and the solvent removed by distillation. The resulting oil was mixed with dilute hydrochloric acid, and extracted with ether to remove the unchanged ethyl γ-phenoxyethylmalonate, then made alkaline with sodium carbonate, and extracted with ether. The basic esters thus obtained amounted to 11 grams, and were mixed with a solution of 4 grams of oxalic acid in 50 c.c. of hot water. This liquor deposited a heavy oil on cooling, and when nearly cold the aqueous layer was poured off from the oil and kept overnight, when it deposited 0·5 gram of *ethyl* 4(or 5)-*glyoxalinemethyl-γ-phenoxyethylmalonate hydrogen oxalate* in clusters of plates melting at 53—55° (corr.). The oil was stirred with water, and kept, when it became mainly crystalline, and the product was collected and dried in the air, when 7 grams of a somewhat viscid, crystalline mass, melting at 45—50°, were obtained. On attempting to recrystallise this from water, a large proportion always separated first as an oil, the liquors then depositing small amounts of the well crystallised salt.

Ethyl 4(or 5)-*glyoxalinemethyl-γ-phenoxyethylmalonate hydrogen oxalate* crystallises from water in clusters of plates melting at 53—55° (corr.). It is sparingly soluble in cold water, and contains a molecule of water of crystallisation:

0·1534 * gave 0·3003 CO_2 and 0·0834 H_2O. C=53·4; H=6·1.
0·2068 * „ 10·8 c.c. N_2 at 16° and 761 mm. N=6·2.
0·1660 * lost 0·0058 in a vacuum over H_2SO_4. H_2O=3·5.
$C_{19}H_{24}O_5N_2,C_2H_2O_4,H_2O$ requires C=53·8; H=6·0; N=6·0; H_2O=3·9 per cent.
0·1428 † gave 0·2914 CO_2 and 0·0742 H_2O. C=55·7; H=5·8.
$C_{19}H_{24}O_5N_2,C_2H_2O_4$ requires C=56·0; H=5·8 per cent.

The base, regenerated from this salt by means of sodium carbonate and ether, was found to yield the lactone of α(β-hydroxyethyl)β-glyoxaline-4(or 5)-propionic acid on treatment with concentrated hydrochloric acid at 150°. For the preparation of the lactone, however, it is unnecessary to isolate the ethyl 4(or 5)-glyoxalinemethyl-γ-phenoxyethylmalonate, the following method giving satisfactory results.

Lactone of α(β-Hydroxyethyl)β-glyoxaline-4(or 5)-*propionic Acid*,



$$\begin{array}{llll} CH_2\cdot & CH\cdot CH_2\cdot & C\cdot NH & \\ | & | & \| & >CH. \\ CH_2 & CO & CH\cdot N & \\ & \diagdown\ \diagup & & \\ & O & & \end{array}$$

Twenty-one grams of 4(or 5)-chloromethylglyoxaline hydrochloride were condensed with 75 grams of ethyl γ-phenoxyethylmalonate by means of 6·1 grams of sodium, and the resulting crude basic esters were isolated as previously described, except that they were extracted by means of chloroform instead of ether. Without further purification, this oil, which amounted to 30 grams, was made up to a volume of 160 c.c. with concentrated hydrochloric acid, and heated at 150° for three hours in sealed tubes. On cooling, a quantity of phenol separated; this was removed by ether, and amounted to about 6 grams. The liquor was then evaporated to dryness under diminished pressure to remove the excess of hydrochloric acid. The residue was dissolved in 100 c.c. of water, and poured into a hot solution of 30 grams of picric acid in 1·5 litres of water. On cooling, a viscid, orange oil separated rapidly, and by the time the solution had cooled to about 50° this separation was almost complete. On then decanting the warm solution through a moistened filter, a clear filtrate was obtained, which almost immediately deposited crystals of the *picrate* of the *lactone* of *α(β-hydroxyethyl)β-glyoxaline*-4(or 5)-*propionic acid.* Further quantities of this picrate were obtained by extracting the amorphous picrates with warm water, and after recrystallisation from water 20·5 grams of the pure salt were obtained. This yield amounts to 38 per cent. of the theoretical.

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* Air-dried. † Dried in a vacuum.

The *lactone* of *α(β-hydroxyethyl)β-glyoxaline*-4(or 5)-*propionic acid* was isolated by converting its picrate into hydrochloride, rendering the solution alkaline with ammonia, and extracting with chloroform; on the removal of the solvent it occurred as a colourless gum, which soon solidified; it was purified by recrystallisation from acetone. Only a part of the lactone was extracted by chloroform from the ammoniacal solution, part remaining in solution presumably as the ammonium salt of the hydroxy-acid; after boiling the liquor with hydrochloric acid, cooling it, and again adding slight excess of ammonia, further quantities of the lactone could be removed by chloroform.

This base forms colourless, glistening prisms (from acetone), which melt at 110—111° (corr.). It is very readily soluble in water, giving a strongly alkaline solution, very readily so in alcohol or chloroform, fairly easily so in acetone or ethyl acetate, and almost insoluble in ether or benzene:

0·1516 gave 0·3204 CO_2 and 0·0795 H_2O. C=57·6; H=5·9.
0·1932 „ 28·2 c.c. N_2 at 20° and 752 mm. N=16·9.
$C_8H_{10}O_2N_2$ requires C=57·8; H=6·1; N=16·9 per cent.

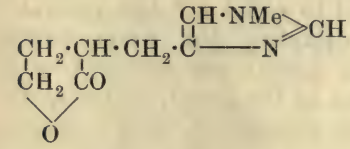
The *hydrochloride* crystallises from absolute alcohol in large, lozenge-shaped prisms, which melt at 136—137° (corr.). It is deliquescent, very readily soluble in water, giving a neutral solution, and easily soluble in absolute alcohol. It is anhydrous:

0·1546 gave 0·2674 CO_2 and 0·0789 H_2O. C=47·2; H=5·7.
0·1571 „ 0·1126 AgCl. Cl=17·7.
$C_8H_{10}O_2N_2$,HCl requires C=47·4; H=5·5; Cl=17·5 per cent.

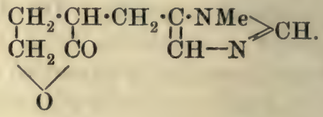
The *picrate* crystallises from water in flat, glistening, deep yellow needles, which melt at 190—191° (corr.). It is anhydrous, and sparingly soluble in cold water:

0·1528 gave 0·2375 CO_2 and 0·0449 H_2O. C=42·4; H=3·3.
0·1024 „ 15·1 c.c. N_2 at 21° and 769 mm. N=17·4.
$C_8H_{10}O_2N_2,C_6H_3O_7N_3$ requires C=42·5; H=3·3; N=17·7 per cent

Lactone of α(β-*Hydroxyethyl*)β-1-*methylglyoxaline*-4(or 5)-*propionic Acid*,



or

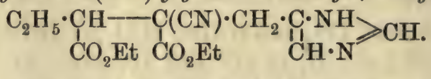


Six grams of the hydrochloride of the lactone of α(β-hydroxyethyl)β-glyoxaline-4(or 5)-propionic acid were dissolved in 50 c.c. of 10 per cent. aqueous sodium hydroxide, and shaken with 6 grams of methyl sulphate. The solution was acidified with hydrochloric acid, and evaporated to low bulk, then made alkaline with ammonia, and extracted with chloroform, this process being twice repeated. The combined chloroform extracts gave 3·0 grams of brown oil. This was converted into the picrate and recrystallised from alcohol, when there were obtained besides considerable quantities of amorphous picrate, and of the picrate of the not methylated lactone, 1·2 grams of the picrate of one of the *N*-methyl derivatives.

The *picrate* of the *lactone* of α(β-*hydroxyethyl*)β-1-*methylglyoxaline*-4(or 5)-*propionic acid* crystallises from alcohol in clusters of long, flat needles, which melt at 158° (corr.), after sintering a few degrees earlier. This salt is sparingly soluble in water or alcohol:

0·1476 gave 0·2370 CO_2 and 0·0479 H_2O. C=43·8; H=3·6.
$C_9H_{12}O_2N_2,C_6H_3O_7N_3$ requires C=44·0; H=3·7 per cent.

Ethyl α-*Cyano*-α-4(or 5)-*glyoxalinemethyl*-β-*ethylsuccinate*,



$$C_2H_5\cdot \underset{CO_2Et}{CH}-\underset{CO_2Et}{C}(CN)\cdot CH_2\cdot \underset{CH\cdot N}{C\cdot NH} > CH.$$

Forty-six grams of ethyl α-cyano-β-ethylsuccinate (Jowett, Trans., 1901, **79**, 1348) were added to a solution of 4·6 grams of sodium in 75 c.c. of absolute alcohol, and the cooled liquid mixed with 15·3 grams of 4(or 5)-chloromethylglyoxaline hydrochloride dissolved in 75 c.c. of absolute alcohol. After boiling for two hours on the water-bath, the alcohol was distilled off, and the residue mixed with an excess of dilute hydrochloric acid. The neutral esters were then removed by extraction with ether, and the liquid made strongly alkaline with sodium carbonate, when the basic esters were extracted by ether. After the removal of the solvent, about 30 grams of basic oil remained, and this was dissolved in 125 c.c. of 10 per cent. aqueous oxalic acid, treated with animal charcoal, and allowed to crystallise, when *ethyl α-cyano-α-*4(or 5)*-glyoxaline-methyl-β-ethylsuccinate hydrogen oxalate* separated. This was recrystallised from 30 c.c. of water, when 11·6 grams of the pure salt melting at 125—128° (corr.) were obtained. On concentrating the original mother liquor a further quantity of the crystalline oxalate separated, and after recrystallisation another 3·8 grams of slightly lower melting point were obtained. The total yield of the crystalline oxalate—15·4 grams—amounted to 39 per cent. of the theoretical.

The original mother liquors which now no longer deposited crystalline matter were diluted with water, and the base was regenerated by means of sodium carbonate and ether, when about 15 grams of basic oil (A) were obtained.

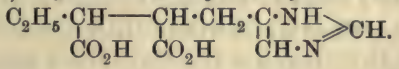
The crystalline *ethyl α-cyano-α-*4(or 5)*-glyoxalinemethyl-β-ethyl-succinate hydrogen oxalate* separates from water in glistening leaflets, which melt at 125—128° (corr.). It is anhydrous, and is sparingly soluble in cold, but readily so in hot, water:

0·2044 gave 0·3816 CO_2 and 0·1084 H_2O. C=50·9; H=5·9.
0·1036 „ 9·5 c.c. N_2 at 25° and 763 mm. N=10·6.
$C_{15}H_{21}O_4N_3,C_2H_2O_4$ requires C=51·3; H=5·8; N=10·6 per cent.

The *base* was regenerated from this salt by means of sodium carbonate and ether. It crystallises from ether in beautiful, large, clear, transparent prisms, which melt sharply at 105—106° (corr.). It is very sparingly soluble in cold water or light petroleum, sparingly so in ether or benzene, and very readily so in the other usual organic solvents:

0·1643 gave 0·3520 CO_2 and 0·1013 H_2O. C=58·4; H=6·9.
0·1141 „ 13·6 c.c. N_2 at 25° and 765 mm. N=13·8.
$C_{15}H_{21}O_4N_3$ requires C=58·7; H=6·9; N=13·7 per cent.

α-4(or 5)*-Glyoxalinemethyl-β-ethylsuccinic Acid,*



$$\begin{array}{l} C_2H_5\cdot\underset{\displaystyle CO_2H}{\underset{|}{CH}}\text{——}\underset{\displaystyle CO_2H}{\underset{|}{CH}}\cdot CH_2\cdot\begin{array}{c} C\cdot NH \\ \| \\ CH\cdot N \end{array}\!\!\gg CH. \end{array}$$

The crystalline oxalate obtained in the previous experiment (15·4 grams) was converted into the base, and this boiled for one and a-half hours under a reflux condenser with 100 c.c. of concentrated hydrochloric acid. The liquor was then evaporated to dryness under diminished pressure, digested with 20 c.c. of absolute alcohol, and filtered from ammonium chloride (0·8 gram). The alcohol was then removed, and the residue dissolved in 1 litre of boiling water, agitated with the silver carbonate from 10 grams of silver nitrate, filtered from the silver chloride, treated with hydrogen sulphide, and again filtered. The solution was then evaporated to dryness under diminished pressure, when 8·0 grams of a nearly colourless varnish remained. This was dissolved in about 20 c.c. of absolute alcohol, and kept, when 1·6 grams of α-4(or 5)-*glyoxalinemethyl-β-ethylsuccinic acid* melting at 220—225° separated. The mother liquor gave no more crystalline matter; it was then again boiled for an hour with concentrated hydrochloric acid, and the above process for the isolation of the free crystalline acid repeated, but still gave no more crystals. The residue was then esterified by means of absolute alcoholic hydrogen chloride, and the esters obtained converted into the acid oxalates and crystallised from water, when a mixture of crystalline oxalates was obtained.

By fractional crystallisation from water a small quantity of a salt was separated, which melted at 133—135° (corr.), gave on analysis figures ($C=51·7$; $H=6·7$) agreeing for the ester oxalate, and when mixed with the pure ester oxalate [m. p. 137—139° (corr.)] melted at 135—138° (corr.).

The oily ethyl α-cyano-α-4(or 5)-glyoxalinemethyl-β-ethylsuccinate (A, p. 539), amounting to 15 grams, was then hydrolysed, and treated in the same way as the crystalline ester, when a very similar result was obtained. The ammonium chloride separated amounted to 0·9 gram, the crude acids to 10·1 grams, the crystalline acid to 1·55 grams, m. p. 220—225°, and on esterifying the residue a similar mixture resulted.

The crystalline and oily cyano-esters therefore appear to yield on hydrolysis the same mixture of acids in the same proportion.

α-4(or 5)-*Glyoxalinemethyl-β-ethylsuccinic acid*, prepared from either the crystalline or oily cyano-ester and crystallised from water, melts and decomposes at 236° (corr.), and a mixture of the acids from the two sources at the same temperature. It crystallises in crusts formed of clusters of glistening needles. It is anhydrous, and is sparingly soluble in cold, although readily so in hot, water, and very sparingly soluble in alcohol:

0·0921 gave 0·1783 CO_2 and 0·0513 H_2O. $C=52·8$; $H=6·2$.

$C_{10}H_{14}O_4N_2$ requires $C=53·0$; $H=6·3$ per cent.

Ethyl α-4(or 5)-*Glyoxalinemethyl-β-ethylsuccinate*, $CO_2Et\cdot CHEt\cdot CH(CO_2Et)\cdot CH_2\cdot C_3H_3N_2$.

Five grams of the acid (m. p. 236°) were boiled with 50 c.c. of absolute alcohol and 50 c.c. of cold saturated absolute alcoholic hydrogen chloride for four hours. The alcohol was then removed, and the residue dissolved in water, made alkaline with sodium carbonate, and extracted with ether.

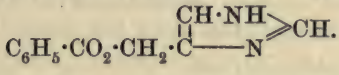
The crude ester, 6·2 grams, was converted into the acid oxalate, and crystallised from water, when 4·8 grams of the pure salt were readily obtained.

The *hydrogen oxalate* crystallises from water in hard clusters of quadrilateral plates, which melt at 137—139° (corr.). It is readily soluble in hot, sparingly so in cold, water, and is anhydrous:

0·1512 gave 0·2852 CO_2 and 0·0904 H_2O. $C=51·4$; $H=6·7$.

$C_{14}H_{22}O_4N_2,C_2H_2O_4$ requires $C=51·6$; $H=6·5$ per cent.

4(or 5)-*Glyoxalinemethyl Benzoate*,



$$C_6H_5\cdot CO_2\cdot CH_2\cdot\begin{array}{l}CH\cdot NH\\ \|\\ C\text{——}N\end{array}\!\!>CH.$$

Ten grams of 4(or 5)-hydroxymethylglyoxaline (Trans., 1911, **99**, 673) and 14·5 grams of benzoyl chloride were stirred together; heat was generated, and the base melted and became a gummy mass. The mixture was digested for half-an-hour in the steam-bath with occasional stirring, and gradually became a chalky, crystalline mass. This was dissolved in water, filtered from a little insoluble matter, extracted with ether to remove impurities, and decolorised by means of animal charcoal. The clear solution was then made alkaline with ammonia, when 4(or 5)-glyoxalinemethyl benzoate separated as an oil, which readily became a sandy, crystalline powder on stirring. This product melted at 140°, and amounted to 13·2 grams, that is, 64 per cent. of the theoretical yield.

4(or 5)-*Glyoxalinemethyl benzoate* crystallises from alcohol in prisms, which melt at 140—141° (corr.). It is insoluble in water, but soluble in dilute acids. It is insoluble in aqueous sodium carbonate or ammonia, but dissolves in cold dilute aqueous sodium hydroxide, decomposing and forming a yellowish-brown solution, from which on acidifying benzoic acid separates. Like all glyoxalines containing an unsubstituted imino-group, it gives an intense red coloration with sodium diazobenzene-*p*-sulphonate; this indicates that the hydroxy- and not the imino-group is the point of attachment of the benzoyl group. It is readily soluble in cold alcohol, very readily so in hot alcohol, and fairly easily soluble in chloroform or ether:

0·1354 gave 0·3230 CO_2 and 0·0616 H_2O. C=65·1; H=5·1.
$C_{11}H_{10}O_2N_2$ requires C=65·3; H=5·0 per cent.

The *hydrochloride* crystallises from absolute alcohol in clusters of long, flat needles, which melt at 183—184° (corr.). It is very readily soluble in water, giving an acid solution, readily so in hot absolute alcohol, but sparingly so in cold absolute alcohol:

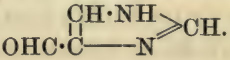
0·1633 gave 0·3290 CO_2 and 0·0692 H_2O. C=54·9; H=4·7.
0·1372 „ 0·0810 AgCl. Cl=14·6.
$C_{11}H_{10}O_2N_2,HCl$ requires C=55·3; H=4·7; Cl=14·9 per cent.

4(or 5)-*Glyoxalinemethyl* p-*Nitrobenzoate*,
$NO_2\cdot C_6H_4\cdot CO_2\cdot CH_2\cdot C_3H_3N_2$,

was prepared by heating together 4(or 5)-hydroxymethylglyoxaline and *p*-nitrobenzoyl chloride for one hour at 130°, and isolated in a manner similar to that employed in the case of 4(or 5)-glyoxalinemethyl benzoate. It crystallises from alcohol in prisms, which melt at 106—107° (corr.). It is insoluble in water, readily soluble in cold alcohol, and very readily so in hot alcohol:

0·1623[*] gave 0·3168 CO_2 and 0·0528 H_2O. C=53·2; H=3·6.
$C_{11}H_9O_4N_3$ requires C=53·4; H=3·7 per cent.

4(or 5)-*Glyoxalineformaldehyde*,



$$\begin{matrix} & CH\cdot NH & \\ & \| & >CH. \\ OHC\cdot & C\text{———}N & \end{matrix}$$

Five grams of 4(or 5)-hydroxymethylglyoxaline were dissolved in 100 c.c. of 10 per cent. sulphuric acid, mixed with 3·5 grams of chromium trioxide, and the mixture heated on a steam-bath for an hour; the liquor was mixed with excess of aqueous sodium carbonate, evaporated to dryness in a vacuum, and the residue extracted with alcohol. After removing the solvent at a low temperature, a syrup remained, which became partly crystalline on keeping; the crystals were collected and recrystallised from a little water, when 0·7 gram of the base was obtained.

4(or 5)-*Glyoxalineformaldehyde* crystallises from water in irregular leaflets, which melt at 173—174° (corr.). It is somewhat sparingly soluble in cold, readily so in hot, water:

0·1864 gave 0·3416 CO_2 and 0·0717 H_2O. C=50·0; H=4·3.
$C_4H_4ON_2$ requires C=50·0; H=4·2 per cent.

The *hydrogen oxalate* separates from water in irregular grains, which decompose at 191° (corr.). It is sparingly soluble in cold, easily so in hot, water.

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[*] Dried at 100°.

The *picrate* formed striated broken rods (from water), which melt at 195—196° (corr.). It is sparingly soluble in cold, readily so in hot, water:

0·1426 * gave 0·1916 CO_2 and 0·0286 H_2O. C = 36·6; H = 2·2.

$C_4H_4ON_2,C_6H_3O_7N_3$ requires C = 36·9; H = 2·2 per cent.

4(or 5)-β-*Aminoethylglyoxaline.*

Although a considerable number of salts of 4(or 5)-β-aminoethylglyoxaline have previously been described by Windaus and Vogt (*Ber.*, 1907, **40**, 3691) and Ewins and Pyman (Trans., 1911, **99**, 339), the free base has not hitherto been obtained in crystalline form. It may be readily isolated by mixing an aqueous solution of a pure salt (dihydrobromide or di-acid phosphate) with excess of sodium carbonate, evaporating completely dry in a vacuum, and extracting with hot chloroform. The extract is dried with sodium hydroxide, and evaporated to low bulk, when on keeping the base crystallises in clear, colourless, wedge-shaped plates, which melt at 83—84° (corr.), after softening a few degrees earlier.

After drying in a vacuum over sulphuric acid:

0·1878 gave 0·3694 CO_2 and 0·1386 H_2O. C = 53·6; H = 8·3.

$C_5H_9N_3$ requires C = 54·0; H = 8·2 per cent.

This base is very deliquescent, very readily soluble in water or alcohol, readily so in hot chloroform, but sparingly so in cold chloroform, and practically insoluble in dry ether. It distils at 209—210°/18 mm., passing over as a very viscous, colourless oil, which solidifies on seeding, forming a crystalline mass melting at 82—83° (corr.); a small proportion of coloured residue remains in the distillation flask.

The *monohydrobromide* crystallises from absolute alcohol in prismatic rods, which melt at 182—183° (corr.). It is anhydrous, readily soluble in water, giving a strongly alkaline solution, but sparingly soluble in cold absolute alcohol:

0·1290 gave 0·1492 CO_2 and 0·0630 H_2O. C = 31·5; H = 5·5.

$C_5H_9N_3,HBr$ requires C = 31·2; H = 5·3 per cent.

The *di-acid phosphate*, $C_5H_9N_3,2H_3PO_4$, is particularly suitable for the characterisation and purification of 4(or 5)-β-aminoethylglyoxaline on account of its crystalline form and sparing solubility in water. It separates from water in magnificent, clear, colourless, quadrilateral prisms belonging to the monoclinic system; the prisms are almost completely capped by a pair of pyramid faces, but a diminutive second pair is nearly always present, and usually a basal plane; orthopinacoid and clinopinacoid faces are sometimes present, and crystals very closely resembling augite in form have been observed. Crystals half-an-inch long and nearly a quarter-of-an-inch broad are deposited from solutions containing only a few grams. This salt melts at 132—133° (corr.) after sintering earlier, and is anhydrous. It is soluble in about four parts of cold water, but readily so in hot water:

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* Dried at 100°.

0·1836 gave 20·8 c.c. N_2 at 12° and 763 mm. $N=13·7$.
0·2028 „ 0·1460 $Mg_2P_2O_7$. $PO_4=61·4$.
$C_5H_9N_3,2H_3PO_4$ requires $N=13·7$; $PO_4=61·9$ per cent.

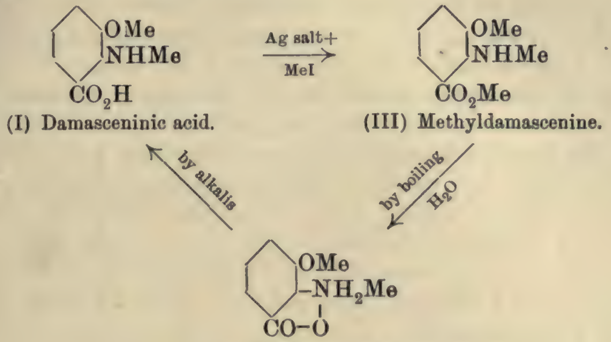
WELLCOME CHEMICAL WORKS,
DARTFORD, KENT.

LXII.—*The Constitution and Synthesis of Damascenine, the Alkaloid of Nigella damascena.*

By ARTHUR JAMES EWINS.

THE alkaloid damascenine was first isolated by Schneider (*Pharm. Centr.-h.*, 1890, **31**, 173) from the seeds of *Nigella damascena.* He described it as a crystalline solid melting at 27°, and assigned to it the composition $C_{10}H_{15}O_3N$. This work is now shown to be substantially correct, the composition of the alkaloid being actually represented by the formula $C_{10}H_{13}O_3N$, differing only from the former in having two hydrogen atoms less. Until now, however, the work of Schneider has been obscured by the results of Pommerehne, who assigned to the alkaloid the formula $C_9H_{11}O_3N$ (*Arch. Pharm.*, 1900, **238**, 531), and stated that it was readily converted by alkalis into an isomeric acid, damasceninic acid. This formula was, moreover, accepted by Keller (*Arch. Pharm.*, 1904, **242**, 299), who later (*ibid.*, 1908, **246**, 1) obtained an alkaloid from *Nigella aristata* having the composition $C_{10}H_{13}O_3N$, which he termed "methyldamascenine." As will be shown later, however, this is the only alkaloid present in *Nigella*, and is identical with Schneider's damascenine.

The constitution of damasceninic acid, which is readily formed from damascenine, was, however, fairly conclusively shown by Keller to be 2-methylamino-3-methoxybenzoic acid (I), the synthesis of which he unsuccessfully attempted. From this acid "methyldamascenine" (III) was obtainable, but in order to explain the supposed isomerism of the acid with damascenine a betaine-like structure (II) was suggested, which involves a quinquevalent nitrogen atom linked in a manner which is without analogy, and is, as will be shown below, also without experimental foundation. The suggested relationship for the supposed three compounds is shown by the following scheme:



(I) Damasceninic acid.

(III) Methyldamascenine.

(II) Damascenine.

It was the doubt attaching to Keller's "betaine" formula which first suggested the present investigation. Since damasceninic acid could be converted into damascenine, the synthesis of the former was first attempted. Keller, starting from 3-nitromethylanthranilic acid, failed to achieve the synthesis; but it was accomplished with very little difficulty in the present instance by starting from *m*-hydroxybenzoic acid. The successive reactions employed will be referred to later. It was then somewhat unexpectedly found that the methyl ester of damasceninic acid was in all respects identical with the alkaloid damascenine as described by Schneider, and found by the author to be the only alkaloid obtainable from *Nigella damascena.*

In view of this result it was only necessary to explain some of the results obtained by Pommerehne and by Keller. The explanation becomes obvious if it is borne in mind that damascenine, now shown to be the methyl ester of an amino-acid, is very readily hydrolysed. Pommerehne himself (*Arch. Pharm.*, 1899, **237**, 475) emphasised the similarity of damascenine to the ester of anthranilic acid. Nevertheless, in the preparation of the hydrochloride of the alkaloid he evaporated a hydrochloric acid solution of the base at temperatures as high as 80° to 90°. The salt which he thus obtained, and which both he and Keller considered to be the hydrochloride of damascenine, was in reality a mixture consisting largely of the hydrochloride of damasceninic acid, and their conclusion that both damascenine and damasceninic acid had the same formula is consequently not surprising. That this is the explanation of many of their observations is clear when we consider some of these more closely; for example, Pommerehne was able to obtain only a small quantity (about 20 per cent.) of the theoretical amount of base from his hydrochloride. The numerous analyses of this salt, too, are by no means concordant. The difficulty of separation of such a mixture, too, is emphasised by Keller himself (*Arch. Pharm.*, 1908, **246**, 1), who by very careful fractionation of a hydrochloride obtained from *Nigella aristata* succeeded in obtaining a small quantity of the hydrochloride of the unchanged alkaloid (which he erroneously considered to be "methyldamascenine"), the greater part of the alkaloid having undergone hydrolysis, and yielded the impure mixture first obtained by Pommerehne. Further, Keller found that methyl iodide, acetic anhydride, acetyl chloride, and nitrous acid produced identical products from both damasceninic acid and the so-called damascenine hydrochloride, a result which he considered to be due to intramolecular rearrangement brought about by these reagents.

The identity of the two substances might have been suspected from the similarity in melting points of a number of salts of the two substances which are included in the following table, which also shows the identity of the synthetic compounds obtained in this investigation with those of the natural alkaloid described by Schneider or by the present author:

	Damascenine.				Damasceninic acid.			
	Natural alkaloid. (Schneider)	"Methyl-damascenine." (Keller)	Natural alkaloid. (Ewins)	Synthetic alkaloid. (Ewins)	Damasceninic acid. (Pommerehne)	"Damascenine." (Pommerehne)	Damascenic acid (natural). (Ewins)	Synthetic. (Ewins)
Base	27°	—	24–26°	23–24°	78° * 140–141°†	— —	— —	72–77° 141–142°
Hydrochloride (anhydrous)	—	—	156°	156°	209–210°	—	210–211°	210–211°
Hydrochloride + H_2O	121°	121°	122°	122°	—	197°		
Sulphate	168–170°	—	168–170°	168–169°	209–210°	203–205°	—	
Nitrate	98°	—	94–95°	94–95°	—	180°	—	
Hydrobromide	—	—	—	—	204–206°	197–199°	—	
Picrate	—	—	159°	159°	190°	189–190°	190°	190°
Platinichloride	165° ?	198°	193–194°	194°	202–203°	198°	201–202°	202°

* Acid + $3H_2O$. † Acid (anhydrous).

Synthesis of Damascenine.—This was accomplished by the following series of reactions. *m*-Hydroxybenzoic acid was converted into *m*-methoxybenzoic acid (m. p. 108°) by methyl sulphate and potassium hydroxide, the yield being practically quantitative. This acid on nitration under suitable conditions gave a mixture of nitro-derivatives, from which the required 2-nitro-3-methoxybenzoic acid was isolated without difficulty. This on reduction yielded 2-amino-3-methoxybenzoic acid, which on treatment with methyl iodide yielded the hydriodide of 2-methylamino-3-methoxybenzoic acid. This salt was converted into the corresponding hydrochloride, which was found to be identical with the hydrochloride of damasceninic acid. Keller's suggested constitution for the latter was thus confirmed. The acid on esterifying by Fischer's method gave a methyl ester, which proved to be identical with the natural alkaloid damascenine.

The steps in the synthesis are shown by the following scheme:

m-Hydroxybenzoic acid.
↓
m-Methoxybenzoic acid.
↓
2-Nitro-3-methoxybenzoic acid.
↓
2-Amino-3-methoxybenzoic acid.
↓
2-Methylamino-3-methoxybenzoic acid.
↓
Methyl 2-methylamino-3-methoxybenzoate (damascenine).

EXPERIMENTAL.

(a) *Preparation of Damascenine from the Seeds of* Nigella damascena.

Three kilograms of the finely ground seeds were extracted with light petroleum by shaking for some time and then filtering, and finally pressing out through fine muslin. The process was repeated until the extract on shaking with dilute acid gave a solution which no longer showed alkaloidal reactions. The petroleum extracts were combined and extracted with a 5 per cent. solution of hydrochloric acid. It is not advisable to concentrate the petroleum extract to any great extent, as in that case on shaking with dilute acid a troublesome emulsion is produced, and separation is effected only with difficulty. By directly extracting as described above, this difficulty is avoided. When all the alkaloid had been removed from the petroleum solution, the acid liquid was rendered alkaline by addition of solid sodium carbonate (the temperature being kept low by cooling in ice-water), and the oily precipitate which then formed extracted by shaking with ether. The ethereal solution was washed with water, dried, filtered, the solvent removed, and the yellow, oily residue distilled under diminished pressure. It distilled almost completely, and boiled constantly at 154°/15 mm. The pale yellow, oily liquid thus obtained was placed in a freezing mixture, when it solidified to a crystalline mass, which melted at 24—26°. Yield, 9·5 grams, or 0·32 per cent. of the seeds employed:

0·1092 gave 0·2466 CO_2 and 0·0660 H_2O. C=61·6; H=6·7.
0·1258 „ 8·8 c.c. N_2 (moist) at 19° and 740 mm. N=7·8.
$C_{10}H_{13}O_3N$ requires C=61·5; H=6·6; N=7·2 per cent.

The alkaloid boils at about 270°/750 mm. with slight decomposition. Its solutions in organic solvents show a very beautiful, blue fluorescence. The alkaloid so obtained agreed completely with the description of the base as given originally by Schneider (*loc. cit.*).

(*b*) *Synthesis of Damascenine.*

Methylation of m-*Hydroxybenzoic Acid.*—Fifty grams of *m*-hydroxybenzoic acid were dissolved in 200 c.c. of methyl alcohol, and a solution of 30 grams of sodium hydroxide in a minimum quantity of water was added. The mixture was then treated with 90 grams of methyl sulphate, when a vigorous reaction ensued. Potassium hydroxide in 50 per cent. aqueous solution was added in small quantities until the reaction became less vigorous. Sixty grams of methyl sulphate were then added in small quantities alternately with the solution of potassium hydroxide. The liquid was set aside for an hour, diluted with four volumes of water, filtered if necessary, and acidified with concentrated hydrochloric acid. The precipitated acid was collected at the end of an hour, and consisted of nearly pure *m*-methoxybenzoic acid melting at 107—108°. The yield was 45·5 grams, or 85 per cent. of the theoretical.

Nitration of m-*Methoxybenzoic Acid.*—To 20 grams of *m*-methoxybenzoic acid were added 80 c.c. of nitric acid (D 1·4). The mixture gradually became warm, the acid slowly dissolved, but almost immediately the mixture of nitro-derivatives began to separate. The temperature of the reaction mixture was never allowed to rise above 60°. Neglect of this precaution leads to a very much more vigorous reaction, and the yield of the required acid is greatly diminished. At the end of about three hours the mixture was diluted with water, the solid collected, and the crude product extracted with a small quantity of boiling alcohol. The less soluble residue was recrystallised from a larger volume of hot absolute alcohol. On cooling, 2-nitro-3-methoxybenzoic acid separated in rhombic plates melting at 249—250°. The acid was identified by analysis (Found, C=48·9; H=3·8; N=7·3. Calc., C=48·7; H=3·5; N=7·1 per cent.), melting point, and general properties with the acid obtained by Rieche (*Ber.*, 1889, **22**, 2352) from 2-nitro-3-methoxybenzaldehyde on oxidation with potassium permanganate.

Reduction of 2-Nitro-3-methoxybenzoic Acid to 2-Amino-3-methoxybenzoic Acid.—Ten grams of 2-nitro-3-methoxybenzoic acid were dissolved in 100 c.c. of absolute alcohol; 18 grams of tin foil and 60 c.c. of concentrated hydrochloric acid were then added alternately in small quantities, and the mixture was finally heated on the water-bath for three hours. The resulting solution was diluted with water, filtered, and the tin removed as sulphide. The filtrate was evaporated to small volume (40 c.c.), and solid sodium carbonate carefully added until the acid reaction to Congo-red just disappeared. After some time the crystalline *2-amino-3-methoxybenzoic acid* separated. It was recrystallised from water, and was then obtained in glistening, feathery clusters of thin plates melting at 162—163°. The yield was 5·15 grams, or 60 per cent. of the theoretical:

0·0744 gave 0·1572 CO_2 and 0·0362 H_2O. C = 57·6; H = 5·4.
0·1197 „ 8·8 c.c. N_2 (moist) at 19° and 761 mm. N = 8·5.
$C_8H_9O_3N$ requires C = 57·5; H = 5·4; N = 8·4 per cent.

2-Amino-3-methoxybenzoic acid is a glistening, crystalline solid, very sparingly soluble in cold, fairly readily so in hot, water. It is readily soluble in alcohol, ethyl acetate, or ether. It may be crystallised from hot benzene, from which it separates on cooling in masses of feathery needles. The solutions of the acid in organic solvents show a well marked blue fluorescence.

The *hydrochloride* is readily obtained by dissolving the acid in hot concentrated hydrochloric acid. On cooling, the hydrochloride separates in glistening, rhombic plates, melting at 204—205°:

0·1100 gave 0·0778 AgCl. Cl = 17·5.
$C_8H_9O_3N,HCl$ requires Cl = 17·4 per cent.

The *picrate* is readily obtained by treating a solution of the hydrochloride in water with a slight excess of a saturated aqueous solution of picric acid. It separates in deep red-coloured needles, melting at 172° to a red liquid:

0·1264 gave 0·1970 CO_2 and 0·0346 H_2O. C = 42·5; H = 3·0.
$C_8H_9O_3N,C_6H_3O_7N_3$ requires C = 42·4; H = 3·0 per cent.

The salt is sparingly soluble in cold, but moderately so in hot, water.

Methylation of 2-Amino-3-methoxybenzoic Acid.—Five grams of 2-amino-3-methoxybenzoic acid were dissolved in 25 c.c. of methyl alcohol, and 4·3 grams (1 molecular proportion) of methyl iodide added. The mixture was heated in a sealed tube for three hours at 100°. The liquid was then evaporated to dryness, the residue dissolved in a little water, and filtered from a small amount of insoluble material. The solution was then digested on the water-bath for an hour with an excess of freshly prepared moist silver chloride. The silver halides were removed by filtration, the filtrate evaporated to dryness, and the residue crystallised from absolute alcohol. There were thus obtained 4·25 grams of the hydrochloride of 2-methylamino-3-methoxybenzoic acid (damasceninic acid), melting sharply at 210—211°:

0·1418 gave 0·2559 CO_2 and 0·0743 H_2O. C = 49·2; H = 5·8.
0·1754 „ 0·1146 AgCl. Cl = 16·2.
$C_9H_{11}O_3N$ requires C = 49·6; H = 5·5; Cl = 16·3 per cent.

The identity of this salt with damasceninic acid hydrochloride was established by the following facts. The melting point of a mixture of equal weights of the synthetic and natural salts showed no lowering of the original temperatures, which were the same in each case. The platinichlorides (m. p. 202—203°) and picrates (m. p. 190°) obtained from both were identical. Further, by dissolving the synthetic hydrochloride in a little water, adding a calculated quantity of sodium carbonate sufficient to neutralise the hydrochloric acid contained in the salt, evaporating to dryness, and extracting with alcohol, a solid was obtained which crystallised from a concentrated aqueous solution and melted somewhat indefinitely from 72° to 77°. The dry solid on crystallisation from a mixture of chloroform and alcohol yielded stout, transparent, rhombic plates, melting at 141—142°, which were very hygroscopic. These properties are in complete agreement with those described by Keller for free damasceninic acid.

Methyl 2-Methylamino-3-methoxybenzoate (*Damascenine*).—Four grams of damasceninic acid hydrochloride were dissolved in 50 c.c. of methyl alcohol, the solution saturated with dry hydrogen chloride, and boiled under a reflux condenser for five hours. The solution was then concentrated and kept for some time, when 0·6 gram of a hydrochloride melting at 210—211° separated. This was collected, the filtrate evaporated to dryness, dissolved in a few c.c. of absolute alcohol, and dry ether added until crystallisation commenced. In this way a further quantity of a salt (1·4 grams) was obtained, melting at 201—202°. Although these salts were apparently almost pure damasceninic acid hydrochloride, both specimens when dissolved in water and the solution rendered alkaline with sodium carbonate were found to be mixed with a certain amount of the hydrochlorides of the methyl ester, as shown by the fact that in both cases a milky appearance was produced, due to the separation of the free ester. This was very marked in the second specimen.

The mother liquors from the crystalline product obtained above were evaporated to dryness and dissolved in a little cold water. The solution was rendered alkaline with sodium carbonate, and the oily precipitate extracted with ether. The ethereal solution (which showed a strongly marked, blue fluorescence) was washed with water until the washings were neutral, and then dried. On evaporating off the ether a residual oil was obtained, which distilled completely, boiling at 156—157°/17 mm. When placed in a freezing mixture the liquid solidified to a crystalline mass, which when pressed between filter paper at about 0° was found to melt at 23—24°:

0·1256 gave 0·2830 CO_2 and 0·0756 H_2O. C = 61·4; H = 6·7.
$C_{10}H_{13}O_3N$ requires C = 61·5; H = 6·6 per cent.

The identity of this synthetic ester with the naturally occurring damascenine was shown by the following facts. The boiling points and melting points of the two compounds are identical. A mixture of the two specimens melted at 23—25°, thus showing no lowering of melting point. Further, the salts obtained from both compounds were in all cases identical with each other and in good agreement with those originally described by Schneider, as shown in the table on p. 546.

Solutions of both compounds gave with mercuric chloride an oily precipitate, which crystallised within a few minutes, as also described by Schneider.

Two new salts of damascenine were obtained during this investigation, namely, the anhydrous hydrochloride and the picrate.

Damascenine Hydrochloride (*Anhydrous*).—This salt was readily prepared by precipitating a dry ethereal solution of the base by careful addition of an alcoholic solution of hydrogen chloride. It crystallises in slender prisms melting at 156°:

0·1490 gave 0·0920 AgCl. Cl = 15·27.
$C_{10}H_{13}O_3N,HCl$ requires 15·33 per cent.

The salt is deliquescent, and when crystallised from 80 per cent. alcoholic solution separates with one molecule of water of crystallisation, then melting at 121—122° as described by Schneider (*loc. cit.*) and by Keller (as "methyldamascenine" hydrochloride). The latter salt does not lose its water of crystallisation when dried in a vacuum over sulphuric acid, but the anhydrous salt may be obtained by carefully heating at 100°.

Damascenine picrate was obtained by precipitating an aqueous solution of a salt of the base with a saturated solution of picric acid in water. It crystallises in lemon-yellow, rhombic plates, melting at 158—159°, and, unlike damasceninic acid picrate, melts without the formation of a blue liquid:

0·1000 gave 0·1664 CO_2 and 0·0332 H_2O. C=45·4; H=3·7.
$C_{10}H_{13}O_3N,C_6H_3O_7N_3$ requires C=45·3; H=3·8 per cent.

The author wishes to express his thanks to Dr. G. Barger, by whom his attention was first drawn to the question dealt with in this investigation.

THE WELLCOME PHYSIOLOGICAL RESEARCH LABORATORIES,
HERNE HILL, S.E.

LXIII.—*Viscosity and Association. Part II. The Viscosity of Geometrical Isomerides.*

By FERDINAND BERNARD THOLE.

SINCE the prediction of geometrical isomerism by van't Hoff and its practical development by Wislicenus, and in the nitrogen series by Hantzsch and Werner, a large number of such isomerides have been prepared, and their chemical transformations have been very thoroughly investigated. On the other hand, information with regard to the physical properties of such substances is very scanty, and in no case have a sufficient number of substances been compared to give any general method of characterising the configuration from a knowledge of a physical property. A summary of the chief investigations on the physical properties of geometrical isomerides is given below.

Fusibility and Solubility.—Michael (*J. pr. Chem.*, 1895, [ii], **52**, 345) has shown that the maleinoid form of ethylenic isomerides is more fusible, more volatile, and more soluble than the fumaroid form.

In the case of the oximes, the *anti*-form has the lower melting point and the greater solubility, but this rule is reversed with certain derivatives such as the ethers. Very little information with regard to the phenylhydrazones is available, but apparently the more soluble form has the lower melting point.

Molecular Volume.—Traube (*Annalen*, 1886, **240**, 43), from measurements on aqueous solutions of sodium maleate, crotonate, and citraconate, and their *trans*-isomerides, concluded that the latter substances possess the greater molecular volume.

Molecular Refractive Power.—According to Perkin (Trans., 1896, **69**, 1145), the magnetic rotations of fumaroid esters are greater than those of the maleinoid compounds.

Absorption of Light.—Magini (*J. Chim. phys.*, 1904, **3**, 403) and Stewart (Trans., 1907, **91**, 199, 1537) have shown that fumaric and mesaconic acids have a greater general absorption than maleic and citraconic acids. The two benzaldoximes, however, give identical absorption spectra (Hartley and Dobbie, Trans., 1900, **77**, 509), whilst of the two camphorquinonephenylhydrazones the β-form shows a greater absorption than the ordinary α-form.

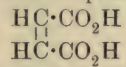
Viscosity.—Lauenstein (*Zeitsch. physikal. Chem.*, 1892, **9**, 422) measured the viscosities of the sodium salts of maleic, fumaric, mesaconic, and citraconic acids in aqueous solution, and calculated the viscosity of the salt by Arrhenius' formula. The results show that sodium maleate is less viscous than the fumarate, whilst with sodium citraconate and mesaconate the reverse holds. No account, however, is taken of ionisation of the salts.

Beck (*Zeitsch. physikal. Chem.*, 1904, **48**, 674) measured the viscosities of a number of fused oximes, and showed that the *syn*-form has a greater viscosity than the *anti*-form, and also that the so-called α′-oximes are hydrates of the ordinary α-form.

Consideration of these results and of those detailed in the present research shows that the physical properties of geometrical isomerides depend on the relative disposition of the groups which may conceivably possess residual affinity.

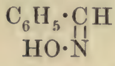
The author therefore proposes in this paper to express the relative positions of these groups by the terms *adjacent* and *opposed*, as embracing the more usual prefixes *cis*, *trans*, *syn*, *anti*, α, and β; for example:

Adjacent compounds.



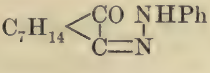
$$\begin{array}{l} \mathrm{HC\cdot CO_2H} \\ \;\,\| \\ \mathrm{HC\cdot CO_2H} \end{array}$$

(*cis*)-Maleic acid.



$$\begin{array}{r} \mathrm{C_6H_5\cdot CH} \\ \| \;\; \\ \mathrm{HO\cdot N} \;\; \end{array}$$

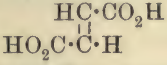
anti-(α)-Benzaldoxime.



$$\mathrm{C_7H_{14}} < \begin{array}{l} \mathrm{CO\;\;NHPh} \\ \;| \qquad\; | \\ \mathrm{C{=}N} \end{array}$$

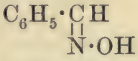
Camphorquinone-β-phenylhydrazone.

Opposed compounds.



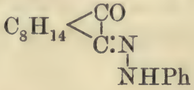
$$\begin{array}{r} \mathrm{HC\cdot CO_2H} \\ \| \qquad \\ \mathrm{HO_2C\cdot C\cdot H} \end{array}$$

(*trans*)-Fumaric acid.



$$\begin{array}{l} \mathrm{C_6H_5\cdot CH} \\ \qquad\;\, \| \\ \qquad\;\, \mathrm{N\cdot OH} \end{array}$$

syn-(β)-Benzaldoxime.



$$\mathrm{C_8H_{14}} < \begin{array}{l} \mathrm{CO} \\ \;| \\ \mathrm{C{:}N} \\ \quad\;\, | \\ \quad\;\, \mathrm{NHPh} \end{array}$$

Camphorquinone-α-phenylhydrazone.

EXPERIMENTAL.

The apparatus and method employed in this work have been fully described in a previous paper (Trans., 1910, **97**, 2597), the viscosities in this series of observations being determined at 24·70°.

The substances used in the research were carefully purified by suitable means, extreme care being necessary in dealing with certain of the more unstable compounds, such as benzaldehyde-β-phenylhydrazone and the acetaldehydephenylhydrazones.

In only a few cases could the viscosities of the pure substances be determined, and therefore, whenever possible, solutions of the substances in amyl acetate were examined. The author has previously shown that amyl acetate is a very suitable solvent for such purposes, as it has a comparatively slight dissociating effect on an associated solute. As the acids of the fumaric series and the phenylhydrazones of camphorquinone are too sparingly soluble in this solvent to give accurate results, methyl alcohol was used as a solvent for the acids and chloroform for the phenylhydrazones.

In each case the viscosity of the solvent and of two solutions of the substance (usually at concentrations of 3 and 7 per cent.) were

Substance.	Configuration.	Solvent.	Viscosity.
Maleic acid	adjacent	methyl alcohol	0·005805
Fumaric acid	opposed	,, ,,	0·005887
Citraconic acid	adjacent	,, ,,	0·005908
Mesaconic acid	opposed	,, ,,	0·005905
Oleic acid	adjacent	amyl acetate	0·009549
Elaidic acid	opposed	,, ,,	0·009740
α-Bromocinnamic acid	,,	,, ,,	0·008717
α-Bromo-*allo*-cinnamic acid	adjacent	,, ,,	0·008674
Ethyl maleate	,,	—	0·03016
,, fumarate	opposed	—	0·02455
,, citraconate	adjacent	—	0·03251
,, mesaconate	opposed	—	0·02399
,, oleate	adjacent	—	0·08948
,, elaidate	opposed	—	0·08175
,, oleate	adjacent	amyl acetate	0·009260
,, elaidate	opposed	,, ,,	0·009144
Benzaldehyde-α-phenylhydrazone	,,	,, ,,	0·008785
Benzaldehyde-β-phenylhydrazone	adjacent	,, ,,	0·008930
Acetaldehyde-α-phenylhydrazone	—	—	0·008353
Acetaldehyde-β-phenylhydrazone	—	—	0·008378
Camphorquinone-α-phenylhydrazone	opposed ?	chloroform	0·006635
Camphorquinone-β-phenylhydrazone	adjacent ?	,,	0 006334
α-Benzaldoxime	,,	amyl acetate	0·008374
β-Benzaldoxime	opposed	,, ,,	0·008433
α-Anisaldoxime	adjacent	,, ,,	0·008640
β-Anisaldoxime	opposed	,, ,,	0·008725
α-Piperonaloxime	adjacent	,, ,,	0·008849
β-Piperonaloxime	opposed	,, ,,	0·009160
α-Benziloxime	adjacent	,, ,,	0·009300
β-Benziloxime	opposed	,, ,,	0·009402

determined, and from the resulting curve the viscosity at a concentration of Mol. wt./40 per cent. was obtained.

The foregoing table summarises the results obtained, the configurations in column 2 being those generally accepted.

Summary of Results.

The Acids.—The results obtained from the four pairs of acids examined show that the adjacent compound has, as a rule, the low viscosity, and also the lower melting point and greater solubility. Citraconic and mesaconic acids appear somewhat abnormal, as the viscosities are practically identical, that of the adjacent acid being slightly the higher.

The Esters.—Whereas in the case of the acids the adjacent form is less viscous, the esters of this form have a higher viscosity than that of the opposed isomerides.

The Oximes.—The viscosities of the oximes of benzaldehyde, anisaldehyde, and piperonal are exactly parallel with those of the acids, the high melting, less soluble form having the higher viscosity. In the case of the benzil monoximes, however, the α-adjacent compound has the lower viscosity, although its melting point is higher than that of the β-oxime. It would have been of interest to compare the ethers of the two isomeric forms, but it is exceedingly difficult to prepare the opposed aldoxime ethers in a sufficiently pure condition.

As, however, the adjacent anisaldoxime methyl ether is a solid melting at 43°, whilst its opposed isomeride is a liquid, it seems probable that the viscosity of the latter would be the lower, a complete parallel with the previously mentioned esters thus existing.

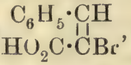
The Phenylhydrazones.—In this case the results are more difficult to interpret, since the general rule of low melting point accompanying low viscosity is no longer obeyed, whilst in one case only (the benzaldehydephenylhydrazones) is the configuration known with any degree of certainty (Ingle and Mann, Trans., 1895, **67**, 606).

Discussion of Results.

Consideration of these results leads to the conclusion that of compounds the constituent radicles of which possess small residual affinity the opposed isomeride has a lower viscosity than the adjacent compound. This result is indeed to be expected, since in the latter isomeride a tendency to potential ring-formation probably exists, a condition which notably enhances viscosity values. On the other hand, when the groups possess a considerable degree of residual affinity, the exaltation of viscosity due to potential ring-formation is masked to a greater or less extent by the depression of viscosity due to intramolecular neutralisation of the residual affinities and consequent inhibition of molecular association.

In Part I. of this series (Trans., 1910, **97**, 2596) the author showed that the viscosities (and therefore the degrees of association) of ortho-substituted phenols were less than those of the meta- and para-isomerides, and, moreover, the degree of association was least when substituents possessing considerable residual affinity were in the ortho-position with respect to the hydroxyl group; for example, the molecular viscosities of *o*-nitrophenol, *o*-chlorophenol, and *o*-cresol are in increasing order of magnitude (199, 212, and 333 respectively). These numbers are closely paralleled by the association factors.

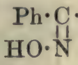
Applying the same considerations to the acids, it might be expected that in maleic acid the residual affinities of the two carboxyl groups would attract each other to such an extent that the depression of viscosity due to inhibition of association would be more than equal to the enhancement of viscosity due to the adjacent arrangement of these groups. The experimental results confirm this theory, for maleic acid has a considerably lower viscosity than fumaric acid. The same explanation accounts for oleic acid being less viscous than elaidic acid, since it is well known that alkyl groups possess a small but appreciable degree of residual affinity. The practical identity of the viscosities of mesaconic and citraconic acids appears at first sight somewhat anomalous, but the presence of the methyl group increases the symmetry of the molecule, thus diminishing the difference between the viscosities of the two isomerides.

Since α-bromo-*allo*-cinnamic acid has a lower viscosity than the isomeride of higher melting point, it probably possesses the adjacent formula  $\begin{array}{c} C_6H_5\cdot CH \\ \quad\;\, \| \\ HO_2C\cdot CBr \end{array}$, a configuration first put forward by Liebermann, and now generally accepted.

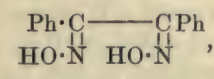
Exactly similar conclusions may be drawn from the viscosities of the oximes. In each case examined the adjacent (*anti* or α) oxime possesses the lower viscosity owing to the partial saturation of the latent affinities of the hydroxyl group by those of the adjacent phenyl residue. As has been previously pointed out, no measurements could be made with the ethers of the oximes, but as the opposed ethers have the lower melting point these compounds are probably exactly analogous with the esters of the ethylenic acids.

Interesting confirmation of this theory is afforded by the fact that barium fumarate crystallises with three molecules of water, whilst the maleate, in which the residual affinities are mutually satisfied, crystallises with one molecule of water.

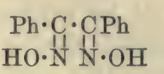
Again, the compounds



$\begin{array}{l}\mathrm{Ph{\cdot}C{\cdot}COPh}\\ \quad\| \\ \mathrm{HO{\cdot}N}\end{array}$,



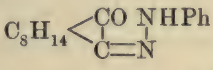
$\begin{array}{l}\mathrm{Ph{\cdot}C\!-\!\!-\!\!-\!\!-\!CPh}\\ \quad\|\qquad\quad\| \\ \mathrm{HO{\cdot}N\ \ HO{\cdot}N}\end{array}$, and



$\begin{array}{l}\mathrm{Ph{\cdot}C{\cdot}CPh}\\ \quad\|\ \ \| \\ \mathrm{HO{\cdot}N\ N{\cdot}OH}\end{array}$

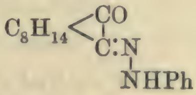
crystallise with alcohol and benzene, whereas the isomerides in which the residual affinities are internally satisfied separate without solvent of crystallisation.

As stated above, the results obtained with the phenylhydrazones are rather more difficult to interpret, as the effect of potential ring-formation in the adjacent compound is nearly equal to the effect due to the internal neutralisation of residual affinity. It is advisable, therefore, to consider separately the three examples investigated. In the case of the two camphorquinonephenylhydrazones:



$\mathrm{C_8H_{14}}{<}\begin{array}{l}\mathrm{CO\ \ NHPh}\\ \mathrm{C{=}N}\end{array}$

and



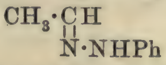
$\mathrm{C_8H_{14}}{<}\begin{array}{l}\mathrm{CO}\\ \mathrm{C{:}N}\\ \quad\mathrm{NHPh}\end{array}$

it is highly probable that the form in which the carbonyl and NHPh groups are adjacent will have the lower viscosity. The low-melting, more soluble form is thus the adjacent compound, a conclusion which agrees with that put forward by Forster and Zimmerli, but which was only based on analogy to other camphor derivatives.

The configurations of the benzaldehydephenylhydrazones have been determined by Ingle and Mann (Trans., 1895, **67**, 606), who find that the low-melting unstable form possesses the adjacent formula. The viscosity of this isomeride is higher than that of the stable opposed form, showing that the effect due to potential ring-formation is greater than that due to inhibition of association.

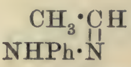
In the case of the acetaldehydephenylhydrazones, the methyl group undoubtedly possesses less residual affinity than the phenyl residue in the benzaldehydephenylhydrazones, and therefore, again, the isomeride possessing the lower viscosity should be the opposed form, the molecular condition now closely resembling that of the esters and oxime ethers.

Since no chemical evidence is available, it may therefore be provisionally stated that the two acetaldehydephenylhydrazones possess the following configurations:



$\begin{array}{l}\mathrm{CH_3{\cdot}CH}\\ \qquad\ \ \|\\ \qquad\ \mathrm{N{\cdot}NHPh}\end{array}$

α-Form, m. p. 98°; stable to alkali.



$\begin{array}{r}\mathrm{CH_3{\cdot}CH}\\ \|\ \ \\ \mathrm{NHPh{\cdot}N}\end{array}$

β-Form, m. p. 56°; stable to acid.

This conclusion is confirmed by the analogy to benzaldehydephenylhydrazone, the adjacent form of which is produced in the presence of acid, and rapidly changes into the opposed compound when treated with alkali hydroxide.

It will be evident that viscosity is a constitutive property of great value, although the important bearing of symmetry and of intramolecular attractions must not be lost sight of in the application of this property to questions of molecular constitution.

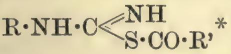
In conclusion, the author desires to express his thanks to Dr. J. T. Hewitt and Dr. M. O. Forster for the interest they have taken in the work, and to the Research Fund Committee of the Chemical Society for a grant which has partly covered the expenses entailed.

East London College.

LXIV.—*Substituted* iso*Thiohydantoins.*

By Augustus Edward Dixon and John Taylor.

When the chloride of a carboxylic acid is brought into contact with a hydrocarbon-monosubstituted thiourea, direct union occurs, the hydrochloride being formed of a basic substance,



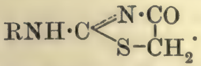
$$\mathrm{R{\cdot}NH{\cdot}C}\!\left\langle\begin{matrix}\mathrm{NH}\\ \mathrm{S{\cdot}CO{\cdot}R'}\end{matrix}\right.{}^{*}$$

in which the acid radicle, $\mathrm{R{\cdot}CO{\cdot}}$, is engaged with the sulphur of the thiourea (Dixon and Hawthorne, Trans., 1907, **91**, 122).

On the other hand, when chloroacetic acid reacts with such a thiourea, the chlorine atom, as before, withdraws the hydrogen of the SH-group, the sulphur of which, engaging with the residue of the acetic acid, forms a so-called "thiohydantoic" acid,

$$\mathrm{RNH{\cdot}C(NH){\cdot}S{\cdot}CH_2{\cdot}CO_2H};$$

by loss of the elements of water, this undergoes, more or less completely, condensation into the *iso*thiohydantoin,



$$\mathrm{RNH{\cdot}C}\!\left\langle\begin{matrix}\mathrm{N{\cdot}CO}\\ \mathrm{S{-}CH_2}\end{matrix}\right..$$

If, however, to a monosubstituted thiourea, chloroacetyl chloride is presented, both the hydrogen atoms are eliminated as hydrogen

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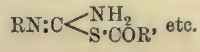
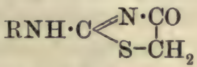
* For the sake of simplicity, no reference is here made to the tautomeric variants, which may (and probably do) exist; for example,

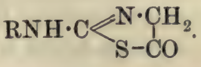


$$\mathrm{RN{:}C}\!\left\langle\begin{matrix}\mathrm{NH_2}\\ \mathrm{S{\cdot}COR'}\end{matrix}\right., \text{ etc.}$$

chloride; in which case the product may obviously possess either of the following constitutions:

(*a*) 

$$RNH\cdot C\!<\!\begin{matrix}N\cdot CO\\ \ \ |\\ S-CH_2\end{matrix}$$

(*b*) 

$$RNH\cdot C\!<\!\begin{matrix}N\cdot CH_2\\ \ \ |\\ S-CO\end{matrix}.$$

Experiment has shown (Dixon and Taylor, Trans., 1908, **93**, 21) that from these and similar materials, at temperatures down to −8°, form (*a*) alone is produced; and hence, of the two groups, $\cdot COCl$ and $\cdot CH_2Cl$, the latter seems preferentially to engage with the SH of a thiourea.

Further, it has been shown (Dixon and Hawthorne, *loc. cit.*, 141) that acid chlorides, $R\cdot COCl$, fail to combine with thioureas containing already an acyl group. If, therefore, chloroacetyl chloride were presented to an acyl trisubstituted thiourea of the form

$$R_2N\cdot C(NAc)\cdot SH,$$

it might be anticipated that a somewhat complex acid chloride would result, as shown by the following equation:

$$R_2N\cdot C(NAc)\cdot SH + ClCH_2\cdot COCl = HCl + R_2N\cdot C(NAc)\cdot S\cdot CH_2\cdot COCl.$$

Experiment has curiously failed to justify this anticipation.

EXPERIMENTAL.

*v-Diphenyl-*n*-benzoylthiourea and Chloroacetyl Chloride.**

These substances, mixed in the proportions required by the equation:

$$Ph_2N\cdot C(N\cdot COPh)\cdot SH + ClCH_2\cdot COCl = Ph_2N\cdot C(N\cdot COPh)\cdot S\cdot CH_2\cdot COCl + HCl,$$

were gently warmed on the water-bath until the solid disappeared. A clear, brown, tenacious, gum-like mass resulted, having the sharp odour of an acid chloride, but possessing also the peculiar characteristic "benzoic" odour. The mass dissolved readily in hot acetone, from which it crystallised on cooling. By recrystallisation from alcohol, brilliant, white prisms were obtained, insoluble in water, sparingly soluble in cold, moderately so in hot, alcohol, and melting at 198° (corr.).

The product, already devoid of chlorine before the recrystallisation from spirit, was not affected by boiling with alkaline solution of lead, and gave but a slight darkening when boiled with ammoniacal silver nitrate; when fused with alkali and nitre, however, it yielded alkali sulphate. As the parent material (Dixon and Taylor, Trans., 1908, **93**, 693) is by no means readily desulphurised by lead salts, the failure of the product to yield its sulphur to alkaline solution of lead was not conclusive evidence that the sulphur had become singly linked in the new molecule. Nevertheless, that this was the case was established by digesting the substance with alcoholic potassium hydroxide; for the residue, when acidified and treated with dilute ferric chloride followed by ammonia, gave Andreasch's reaction for thiolacetic acid, $SH{\cdot}CH_2{\cdot}CO_2H$ (*Ber.*, 1879, **12**, 1385), hence showing the presence of the group $\cdot S{\cdot}CH_2{\cdot}CO\cdot$.

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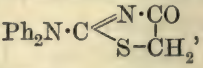
* For nomenclature, see Trans., 1895, **67**, 564.

The conjecture that the above compound was the hitherto unknown *diphenyl*iso*thiohydantoin*,  $Ph_2N{\cdot}C{<}\begin{matrix}N{\cdot}CO\\ |\\ S{-}CH_2\end{matrix}$, was verified by the result of a sulphur determination:

0·3045 gave 0·2670 $BaSO_4$. S = 12·04.

$C_{15}H_{12}ON_2S$ requires S = 11·94 per cent.

*v-Diphenyl-*n*-acetylthiourea and Chloroacetyl Chloride.*

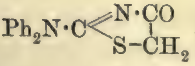
As a check on the foregoing unexpected result, the experiment was repeated, with the above-named materials, and in the same way as before, save that the interaction vessel, surrounded by steam, was provided with a delivery tube dipping into aniline, the object of the latter being to catch the acetyl chloride, if this should be evolved as such. The mixture behaved substantially as in the preceding case, except that gas was evolved; the residue had the pungent odour of acetyl chloride, and by treatment with alcohol gave crystals melting at 198° (corr.).

In every way these resembled the product of the foregoing experiment; and a mixture of the two substances in approximately equal proportions showed no change of melting point.

The aniline had changed to a semi-solid; when treated with hot dilute hydrochloric acid, this yielded a clear solution, from which, on cooling, crystals were deposited. By recrystallisation from water they were obtained in glistening plates, having the appearance of acetanilide, and giving the reactions of this substance.

All these results may be summed up by the equation:

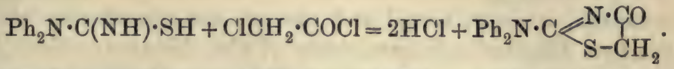
$Ph_2N{\cdot}C(N{\cdot}COMe){\cdot}SH + ClCH_2{\cdot}COCl =$



$$Ph_2N{\cdot}C{<}\begin{matrix}N{\cdot}CO\\ |\\ S{-}CH_2\end{matrix} + HCl + Me{\cdot}COCl.$$

v-Diphenylthiourea and Chloroacetyl Chloride.

A mixture of the two substances in equimolecular proportions, when fused on the water-bath, gave off hydrogen chloride, leaving a clear resin, from which, by crystallisation from alcohol, a product was obtained, indistinguishable in appearance and properties from the compounds already described. Three tubes, charged respectively with (i) the above substance obtained from *v*-diphenylthiourea; (ii) its mixture with that obtained from *n*-benzoyl-*v*-diphenylthiourea; (iii) its mixture with that obtained from *n*-acetyl-*v*-diphenylthiourea, were attached to the same thermometer, and heat was applied; the contents of all three tubes melted simultaneously at 198° (corr.):



$$Ph_2N\cdot C(NH)\cdot SH + ClCH_2\cdot COCl = 2HCl + Ph_2N\cdot C\Big<\begin{matrix}N\cdot CO\\ S-CH_2\end{matrix}.$$

In all the preceding cases the acyl radicle—or the hydrogen atom—displaced from the thiourea was necessarily that attached to the doubly-linked nitrogen atom *; the question now arose whether the expulsion of this radicle depended on its being acidic in function, or whether the withdrawal was conditioned through its being held, initially, in an imino-group. This question, obviously, could be answered by the employment of a thiourea, containing an acyl radicle held in the amino-group, and having the imino-group paralysed by means of a hydrocarbon radicle.

n-*Phenyl-v-carbethoxyphenylthiourea and Chloroacetyl Chloride.*

The above-named thiourea, $Ph(CO_2Et)N\cdot C(NPh)\cdot SH$, obtained first by Seidel from thiocarbanilide and ethyl chlorocarbonate (*J. pr. Chem.*, 1885, [ii], **32**, 263), was melted on the water-bath with 1 molecular proportion of chloroacetyl chloride, and the fusion dissolved in hot acetone; on keeping, a white solid was deposited, which crystallised from alcohol in flattened, vitreous prisms, melting sharply at 176°, insoluble in water, not desulphurised by alkaline salts of lead or of silver, and giving Andreasch's reaction for thiolacetic acid (the parent substance melts at 139°, is readily desulphurised, and does not afford the thiolacetic acid reaction). Analysis was considered unnecessary, the product being, obviously, the diphenyl*iso*thiohydantoin of Lange (*Ber.*, 1879, **12**, 595), melting at 176°.

From the facts now secured, it appears that when chloroacetyl chloride attacks a trisubstituted thiourea having an acyl radicle joined to one of its nitrogen atoms, that radicle is eliminated (as the corresponding chloride), independently of whether it forms part of an amino- or of an imino-group.

As stated earlier, the expulsion by chloroacetyl chloride of the acyl radicle contained in a trisubstituted thiourea is a phenomenon which we did not anticipate. In view, however, of the fact that ring-closing thus occurs, the question naturally presented itself whether, if a thiourea were employed having a hydrogen atom and an acyl radicle both available, the former or the latter would be withdrawn. To test this point, *ab*-acetylphenylthiocarbamide was selected; whatever its static configuration may be, to produce an *iso*thiohydantoin it must interact in the thiourea form; and its substituents, namely, acetyl and phenyl, are respectively attached to the two different nitrogen atoms of the thiourea. Here, therefore, the main issue is simple enough; for an *iso*thiohydantoin, if formed at all, must be either some form of acetylphenyl derivative (if hydrogen only is eliminated) or of a phenyl derivative (if the acetyl radicle is expelled).

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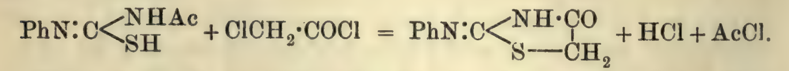
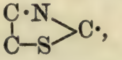
* The "thiourea," of course, might possess originally the thiocarbamidic structure; but, if so, the molecule, to produce an *iso*thiohydantoin, must sooner or later undergo transposition into the thiourea form.

ab-*Acetylphenylthiocarbamide and Chloroacetyl Chloride.*

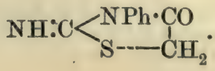
A mixture of these substances, when heated on the water-bath, first liquefied, acetyl chloride and some hydrogen chloride being evolved, and then quickly re-solidified. The nearly white residue, consisting partly of a base and partly of its hydrochloride, was resolved by two recrystallisations from alcohol (which readily withdraws the combined halogen acid) into the base alone. This, when compared with a specimen of phenyl*iso*thiohydantoin made from phenylthiourea and chloroacetyl chloride, was indistinguishable from it in appearance, melting point, and chemical properties. These observations, together with the fact that acetyl chloride is expelled during the interaction, suffice to show the course of the latter, namely:



$$\mathrm{PhN{:}C}{<}\begin{matrix}\mathrm{NHAc}\\ \mathrm{SH}\end{matrix} + \mathrm{ClCH_2{\cdot}COCl} = \mathrm{PhN{:}C}{<}\begin{matrix}\mathrm{NH{\cdot}CO}\\ \mathrm{S{-}{-}CH_2}\end{matrix} + \mathrm{HCl} + \mathrm{AcCl}.$$

Since, in the above interaction, the phenyl and the acetyl radicles are attached originally to different nitrogen atoms, whilst ring-closing is effected through the elimination of the acetyl radicle, it follows that the phenyl radicle lies, so to speak, outside the thiazole ring,  $\begin{matrix}\mathrm{C{\cdot}N}\\ \mathrm{C{-}S}\end{matrix}{>}\mathrm{C}{\cdot}$, a conclusion already reached by one of us on quite different experimental grounds (Dixon, Trans., 1897, **71**, 628).

Isomeric with the *ab*-acetylphenylthiocarbamide referred to above, is the *aa*-form, obtained first by Hugershoff (*Ber.*, 1899, **32**, 3649), and having both the acetyl radicle and the phenyl radicle attached to the same nitrogen atom. Here, then, as it seemed, lay to hand the means of producing the hitherto unknown phenyl*iso*thiohydantoin,



$$\mathrm{NH{:}C}{<}\begin{matrix}\mathrm{NPh{\cdot}CO}\\ \mathrm{S{-}{-}CH_2}\end{matrix}.$$

aa'-*Acetylphenylthiocarbamide and Chloroacetyl Chloride.*

A mixture of these substances—the latter in excess—was fused on the water-bath, the resultant phenomena being in every way similar to those observed in the preceding experiment with the *ab*-compound. Instead, however, of an isomeride, the product was found to consist of ordinary phenyl*iso*thiohydantoin.

An explanation of this seeming discrepancy was not far to seek. for the material actually obtained could not originate directly from the parent substance; at all events, if it contains the group AcPhN·, which there is every reason to believe is the case. Consequently, the genesis from it of an *iso*thiohydantoin, in which the nitrogen atom concerned in the formation of the thiazole ring is not apparently contained in that ring, must be accounted for, either by a preliminary transformation of the *aa*- into the *ab*-thiocarbamide, or else by the assumption that the phenylic radicle at first contained in the ring wanders away from its original attachment and replaces the hydrogen of the external NH-group. For the latter assumption there is no substantial warrant; whereas, for the former, there is the fact that, in various ways, Hugershoff's thiocarbamide may be transformed into the *ab*-isomeride. Now, in the interaction mentioned above, hydrogen chloride is generated, a substance not unlikely to be capable of effecting this change. A direct experiment, made by heating an alcoholic solution of Hugershoff's thiocarbamide with hydrochloric acid on the water-bath, showed the transformation to be practically complete at the end of some four minutes—the time allowed in making the test. Considering the readiness with which the acetyl radicle can move about within the molecule of a thiocarbamide (or thiourea) until it reaches stability in the *ab*-position (Dixon and Hawthorne, *loc. cit.*; Dixon and Taylor, Trans., 1908, **93**, 18), we judge that the production of ordinary phenyl*iso*thiohydantoin from the materials named is due to a wandering of the acetyl radicle of the thiocarbamide, rather than to a migration of the phenyl in a thiohydantoin already formed.

In these circumstances, the prospect of obtaining the isomeric phenyl*iso*thiohydantoin appeared somewhat remote; nevertheless, as the production of this substance would probably serve towards the clearing up of some difficulties in respect of the constitution of the known form, we tried other methods of attacking the unstable acetylphenylthiocarbamide.

The presence of halogen acid being apparently detrimental, we sought first to establish conditions in which, as fast as formed, it would be neutralised. With this object, Hugershoff's thiocarbamide in alcohol was boiled for half-an-hour with a little more than the calculated amount of ethyl monochloroacetate, together with excess of finely-divided calcium carbonate. From the filtrate, on cooling, white crystals were deposited, which proved to be the original thiocarbamide, unchanged; the mother liquor, when tested by Andreasch's method, showed no sign of the presence of thiolacetic acid, and hence presumably contained no *iso*thiohydantoin.

Lest the presence of calcium carbonate might somehow have hindered the desired interaction, the experiment was repeated, but without the addition of the calcium carbonate; the result, however, was precisely the same as before.

Hugershoff's thiocarbamide having failed to yield a thiohydantoin under the above treatment, our next experiment was to boil for an hour a mixture of ethyl chloroacetate with *ab*-acetylphenylthiocarbamide in alcoholic solution; here, also, not a trace of phenyl*iso*thiohydantoin was produced, the acetylphenylthiocarbamide being recovered unchanged from the solution. To make certain that these negative results were not due to any accident, phenylthiourea itself was treated for half-an-hour as before with ethyl chloroacetate; this time the conversion into phenyl*iso*thiohydantoin was practically complete. In this experiment calcium carbonate was present; notwithstanding which, the thiohydantoin separated as usual, that is, partly as free base and partly as hydrochloride. It seems curious that the presence of calcium carbonate should not ensure the removal of the combined hydrogen chloride, whilst the latter is readily eliminated by mere recrystallisation from alcohol.

In the above cases where ethyl chloroacetate failed to interact, the thiourea employed contained an acyl radicle, together with a hydrocarbon radicle; on the other hand, in the case where it interacted, a single hydrocarbon substituent alone was present. Therefore, the failure might be due, either to the presence of an acyl radicle, or, independently of the nature of the radicle, to the fact of two hydrogen atoms in the thiourea being substituted.

To clear up this point the following experiments were made: (1) thiocarbanilide was boiled for half-an-hour with alcohol and ethyl chloroacetate; (2) acetylthiourea was similarly treated. In case (1) the product was Lange's diphenyl*iso*thiohydantoin (see above); it melted at 176°, was not desulphurised by boiling with alkaline lead hydroxide, and gave Andreasch's reaction for thiolacetic acid; thiocarbanilide melts at 151°, is readily desulphurised by hot alkaline lead solution, and does not respond to Andreasch's test. Consequently, the presence of two hydrocarbon radicles in a thiourea is no more a bar against attack by ethyl chloroacetate than is the presence of one such radicle.

Case (2) proved different; some little hydrogen sulphide was evolved during the boiling, but the crystals which separated on cooling were nearly pure acetylthiourea, and the mother liquor from these, when tested by Andreasch's method, gave no reaction whatever for a thiohydantoin.

How the mere presence of an acyl radicle in a substituted thiourea precludes this from reacting with ethyl chloroacetate is not easy to understand.

Acyl substitution derivatives of the *iso*thiohydantoins appear to be unknown; and that no strong tendency exists towards their formation may be inferred from the results with chloroacetyl chloride described at the beginning of this paper; for in those cases where a hydrogen atom and an acyl radicle are equally available in the substituted thiourea, the *iso*thiohydantoin formed is that originating through the elimination, not of hydrogen chloride, but of acetyl chloride, or of some other acyl chloride. That an *iso*thiohydantoin should be acylated with difficulty, or perhaps not at all, or that such an acyl derivative should tend to resist formation, even in circumstances apparently favourable, is probably to be explained by the fact that the *iso*thiohydantoins are by no means strongly basic substances; this might be expected, seeing that they include already the glycolyl complex, $\cdot CH_2\cdot CO\cdot$; and it may well be that the general electronegativeness (if such an expression may be allowed) of these bases has almost reached its limit with their formation, and that further to charge them with negative radicles is difficult, if not impossible. There seems, in fact, to be a fairly distinct limit to the power of thiourea and of its ordinary derivatives to take up acyl radicles; for acyl halides, which unite more or less readily with thiourea, and with its mono-, di-, and tri-substitution derivatives, fail to combine if the thiourea contains an acyl radicle.

In like manner, thiourea or its ordinary substitution derivatives may contain one acyl radicle, but rarely two of these.*

Whilst, however, the above considerations may furnish some reason, at least, for the non-production of acylated thiohydantoins of the class named, on the other hand, there does not appear to be any reason why the ethyl chloroacetate should fail to withdraw the acetyl radicle, seeing that it can so readily eliminate a hydrogen atom. One might even, in fact, anticipate that ethyl acetate would be formed more easily than ethyl alcohol; it is to be remembered, however, that the acetyl radicle has to be dislodged before ethyl acetate can result; and we do not yet know either the relative affinities of acetyl and of hydrogen in the thiourea molecule, or in what precise configurations these radicles are held.

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* Deninger has described (*Ber.*, 1895, **28**, 1322) a 'dibenzoylthiocarbanilide obtained from thiocarbanilide in pyridine solution and benzoyl chloride. This is the only known compound of its class.

From the fact that in the combination of a thiocarbimide, X·NCS, with an amine, $Y{\cdot}NH_2$, the (hydrocarbon) radicles X and Y may be exchanged without influencing the nature of the product, it has been argued by various chemists that the latter must be a symmetrical thiocarbamide, $CS{<}{}^{NHX}_{NHY}$. If this argument is a sound one (which is not quite certain), there is at least some ground for supposing that disubstituted "thiocarbamides" containing an acyl radicle are not similarly constituted; for, whilst acetylthiocarbimide, Ac·NCS, unites with aniline to afford the so-called *ab*-acetylphenylthiocarbamide, yet phenylthiocarbimide shows no tendency whatever to combine with acetamide (or with amides in general). Whatever the real reason for this may be, a possible one is, that the compound under consideration has the formula $AcN{\vdots}C(NHPh){\cdot}SH$. If now, in the union of a thiocarbimide with an amine or an amide, the latter break into the fractions H· and R·NH· (otherwise R·CO·NH·), which thereupon add themselves to the thiocarbimide, X·NCS—the alkyl symmetrically, and the acyl so as to form a thiourea—the first process will run as follows:

$$X{\cdot}NCS + R{\cdot}NH_2 = X{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}R;$$

whereas to produce the thiourea, $R{\cdot}CO{\cdot}N{\vdots}C(NHX){\cdot}SH$, the amide must lose 2H, instead of H, a change which it may not be disposed to undergo. On the other hand, the thiocarbimide, R·CO·NCS, taking up H + XNH, can afford directly $R{\cdot}CO{\cdot}N{\vdots}C(NHX){\cdot}SH$.

It is right to add that this is advanced as a mere conjecture; for, in the first place, the constitution of the acylthioureas (or thiocarbamides) is not yet definitely known, and in the second, the non-interaction of the amides may be due to their general chemical indifference.

The question whether chloroacetyl chloride is able to act directly on *aa*-acetylphenylthiocarbimide remaining still unanswered, we tried the experiment of mixing the two substances dissolved in acetone in presence of a large excess of calcium carbonate. In view of the result already obtained with chloroacetyl chloride and the *ab*-compound (where calcium carbonate failed to deprive the product of its combined halogen acid), the method offered but little hope of success; and in effect, although some effervescence took place, the solid reaction product consisted of a mixture of ordinary phenyl*iso*thiohydantoin with its hydrochloride.

Since the hydrocarbon substituents of a thiourea do not appear to undergo the displacement which occurs so readily when an acyl radicle is present, we next sought to inquire how chloroacetyl chloride would behave towards a thiourea having all its hydrogen, save that of the SH-group, replaced by purely hydrocarbon radicles, X, Y, and Z.

Ring-closing being thus excluded, any interaction that may now take place must occur solely through the withdrawal of the SH-hydrogen, the primary change running on either (or both) of the lines:

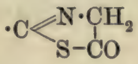
(i) $XYN\cdot C(NZ)\cdot SH + ClCO\cdot CH_2Cl = XYN\cdot C(NZ)\cdot S\cdot CO\cdot CH_2Cl + HCl$;

(ii) $XYN\cdot C(NZ)\cdot SH + ClCH_2\cdot COCl = XYN\cdot C(NZ)\cdot S\cdot CH_2\cdot COCl + HCl$.

In case (ii) the product, being an acid chloride, would probably tend to react with another molecule of the thiourea, so as to afford a compound:

$$XYN\cdot C(NZ)\cdot S\cdot CH_2\cdot CO\cdot S\cdot C(NZ)\cdot NXY.$$

Which of these two reactions would be the more likely to occur, it is not possible to foresee. When the two chlorine atoms of chloroacetyl chloride are presented to the SH-hydrogen of thiourea, or of a monosubstituted, or of a disubstituted thiourea (or even, as now shown, of a trisubstituted thiourea containing an acyl group), that hydrogen picks out, definitely enough, the chlorine of the fraction CH_2Cl; or, rather, it seems to do so; but since in all cases hitherto tested the second chlorine atom is also eliminated with formation of a ring, it is evident that the sulphur atom is not quite free to select between the CH_2 and the CO; in fact, the end result must depend on which of the two configurations:



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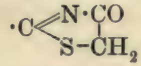

can more easily be formed; and this will depend, not alone on the tendency of S to unite with $\cdot CO\cdot CH_2\cdot$ or $\cdot CH_2\cdot CO\cdot$, as the case may be, but also, conjointly, on the readiness of the nitrogen atom to form the combination $\vdots N\cdot CH_2\cdot$ or $\vdots N\cdot CO\cdot$. In general, the alkyl halides are much less disposed to yield amines than the acyl halides to yield amides; and hence it may reasonably be conjectured that the reason why the sulphur of the thiourea engages with the CH_2 of the chloroacetyl chloride is not so much because the combination $\cdot S\cdot CH_2\cdot$ is more stable than $\cdot S\cdot CO\cdot$, but rather because the nitrogen atom of the thiourea is simultaneously competing for possession of the CO-group.

Neither, in the case of the equations formulated above, is the issue quite a clear one; for in (ii) the product, being an acid chloride, would not be likely to retain the hydrogen chloride formed, whereas in (i) the product, being a kind of base, would probably combine with the eliminated acid, thereby tending to produce, on the whole, a more stable system.

Experiment yielded the results described below.

n-*Phenyl-ν-methylphenylthiourea and Chloroacetyl Chloride.*

The thiourea, PhMeN·C(NPh)·SH (Gebhardt, *Ber.*, 1884, **17**, 2089), dissolved in dry acetone was mixed with 1 molecular proportion of chloroacetyl chloride diluted with the same solvent. No perceptible rise of temperature occurred, but the solution, when concentrated at the ordinary temperature under diminished pressure, yielded a mass of pure, white, glistening needles; these were collected, washed quickly with dry acetone, and dried over sulphuric acid in a vacuum.

The product, rather deliquescent (m. p. about 147°, with evolution of hydrogen chloride), was easily and completely soluble in water, the solution, which was strongly acid, yielding with nitric acid and silver nitrate a white precipitate of silver chloride; further, the original solid, when treated with cold sulphuric acid, evolved fumes of hydrogen chloride.

Moreover, the aqueous solution, on the addition of alkali hydroxide, gave a white precipitate, easily soluble in dilute acid; and when treated with aqueous picric acid yielded a bright, orange-yellow picrate. From these properties it was evident that the white solid was the hydrochloride of a base, presumably (from the method of its formation) $PhMeN\cdot C(NPh)\cdot S\cdot CO\cdot CH_2Cl$; and that the carbon group engaged with the sulphur atom was not $\cdot CH_2\cdot$ was shown by the failure of the substance, when evaporated with alcoholic potassium hydroxide, to afford Andreasch's purple thiolacetic acid reaction:

0·505 required 26·8 c.c. $N/10$-$AgNO_3$. Cl = 18·9.

0·367 gave 0·234 $BaSO_4$. S = 8·76.

$C_{16}H_{16}ON_2ClS,HCl$ requires Cl = 20·00; S = 9·01 per cent.

The lowness of these numbers (which give the ratio $N_2 : S$) is probably due to the retention by the deliquescent salt of a little moisture.

In the circumstances described above, interaction is determined by the union of the SH-hydrogen with the chlorine of the group ·COCl, the group $\cdot CH_2Cl$ apparently remaining unaffected. Nevertheless, there is some reason to believe that the chlorine of the latter group is not quite devoid of power to interact; for when *n*-phenyl-*v*-phenylmethylthiourea was heated directly with chloroacetyl chloride in the absence of any solvent, hydrogen chloride escaped, a deep crimson liquid being formed, which soon solidified. The solid consisted largely of the foregoing hydrochloride, but not entirely so, for it responded very distinctly to Andreasch's test for thiolacetic acid, and hence contained some material having the linking $\cdot S\cdot CH_2\cdot CO\cdot$.

The picrate obtained from the aqueous solution of the hydrochloride, $PhN\colon C(NMePh)\cdot S\cdot CO\cdot CH_2Cl,HCl$, was obtained as an amorphous, rather clotted precipitate; when heated with water it dissolved partly, but with change of colour, suggesting decomposition, and the filtered liquid on cooling gave but a trifling deposit of a solid, which did not seem to be a pure compound. The corresponding hydrochloride, too, is very readily decomposed, an attempt to recrystallise it from 93 per cent. alcohol resulting in the withdrawal of the elements of chloroacetyl chloride and regeneration of the methyldiphenylthiourea. In another experiment, made in the hope of isolating the base, $PhN\colon C(NPhMe)\cdot S\cdot CO\cdot CH_2Cl$, the solution of the hydrochloride in acetone was treated, little by little, with dry calcium carbonate. Until one equivalent had been added the mixture remained clear; but on the addition of a further quantity it became turbid, and continued to effervesce. The brown acid filtrate, when concentrated by slow evaporation, gave a viscid, deep red oil, from which nothing definite could be isolated.

In fact, all the hydrochlorides so far obtained from trisubstituted thioureas appear to possess little stability. Acetyl chloride combined spontaneously in the cold with Gebhardt's methyldiphenylthiourea; but the product formed exceedingly deliquescent crystals, too impure for analysis, and when it was attempted to recrystallise them from alcohol, they decomposed, with regeneration of the original thiourea. Similar results were obtained with ethyl chlorocarbonate.

The general outcome of the present inquiry, and of certain other similar investigations, may now be summarised approximately as follows:

(1) The chlorides, $R\cdot COCl$, of monocarboxylic acids unite directly with thiourea, or with its mono-, di-, or tri-substitution derivatives, to yield substances of the form $XYN\cdot C(NZ)\cdot S\cdot COR,HCl$, X, Y, and Z being hydrogen or hydrocarbon radicles. Whether these are hydrochlorides, containing a quinquevalent nitrogen atom, or sulphonium chlorides is still uncertain.

If the thiourea contains an acyl substituent, such union does not occur.

In the case of thiourea and of its monosubstitution derivatives, withdrawal of the combined halogen acid may be followed by a migration of the acyl radicle to one of the nitrogen atoms of the thiourea. If the thiourea is monosubstituted, the acyl radicle leaving the sulphur tends to migrate first to the nitrogen atom which already holds a hydrocarbon radicle; from this position it may usually be caused to move (and sometimes moves spontaneously) to the other non-substituted nitrogen atom.

(2) Chloroacetyl chloride acts on thiourea and on its hydrocarbon mono- or di-substitution derivatives solely by ring-closing, with production of *iso*thiohydantoins (from the work of various observers, it appears that this is true also of chloroacetic acid).

Thioureas containing an acyl radicle are attacked by chloroacetyl chloride, with expulsion of that radicle (as an acyl chloride), and formation of the corresponding non-acylated *iso*thiohydantoin; but *aa*-acetylphenylthiocarbamide yields the same compound as that obtained from the *ab*-derivative.

Trisubstituted thioureas, including purely hydrocarbon radicles, unite directly with chloroacetyl chloride to form hydrochlorides, $XYN\cdot C(NZ)\cdot S\cdot CO\cdot CH_2Cl,HCl$ (or, possibly, sulphonium chlorides).

(3) Ethyl chloroacetate behaves towards thiourea and towards its hydrocarbon mono- or di-substitution derivatives in the same way as does chloroacetyl chloride. If, however, the thiourea contains an acyl substituent, no interaction takes place.

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LXV.—*Syntheses of* 3-*Oxy*-(1)-*thionaphthen.*

By ARCHIBALD MORITZ HUTCHISON and SAMUEL SMILES.

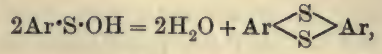
THE characteristic reactions exhibited by solutions of aromatic mercaptans and disulphides in concentrated sulphuric acid have led to the inference (Trans., 1910, **97**, 1290; 1911, **99**, 640) that the sulphoxylic acids are there present. With regard to the formation of these acids evidence has been brought forward to show that they are produced in the acid solutions, either by direct oxidation of the mercaptan:

$$ArSH + H_2SO_4 = ArS\cdot OH + H_2SO_3 \qquad (i)$$

or by hydrolytic fission of the disulphide:

$$ArS\cdot SAr + H_2O \rightleftharpoons ArS\cdot OH + ArSH \qquad (ii)$$

The considerable degree of activity which these solutions exhibit is partly due to a tendency of the sulphoxylic acid to lose oxygen, either directly or in the form of hydroxyl. The chief examples of the latter type of interaction are to be found in the production of thianthrens:



$$2\mathrm{Ar}\cdot\mathrm{S}\cdot\mathrm{OH} = 2\mathrm{H_2O} + \mathrm{Ar}{<}{\substack{\mathrm{S}\\ \mathrm{S}}}{>}\mathrm{Ar},$$

and in the condensations which take place with mercaptans (equation ii) or with aromatic compounds (Trans., 1911, **99**, 640, 1353):

$$\mathrm{ArS}\cdot\mathrm{OH} + \mathrm{HAr'} = \mathrm{H_2O} + \mathrm{ArSAr'},$$

where disulphides and unsymmetrical monosulphides are respectively formed.

In continuing the investigation of the character of these sulphoxylic acids, attention has been directed to the question whether this type of condensation could be effected with other substances containing easily removable hydrogen, and the results now described were obtained with substances embracing the reactive methylene group.

In choosing a mercaptan for use in these experiments the precaution was taken of avoiding those which too readily undergo the intermolecular condensation leading to the thianthrens (Fries and Volk, *Ber.*, 1909, **42**, 1170; Prescott and Smiles, Trans., 1911, **99**, 642), examples of such being the phenyl and *p*-tolyl mercaptans. Other mercaptans unsuitable for the purpose are *o*-amino- or *p*-nitrophenylmercaptans, which with concentrated sulphuric acid give disulphides (equations i and ii) apparently incapable of fission (Prescott and Smiles, *loc. cit.*) into the requisite sulphoxylic acids. In the sulphoxylic acid derived from *o*-thiolbenzoic acid the tendency to these intermolecular condensations is somewhat suppressed, doubtlessly by the ortho-substitution and by the nature of the substituents; hence this mercaptan and the corresponding disulphide have been used in these experiments.

EXPERIMENTAL.

Condensation of o-Thiolbenzoic Acid with Malonic Acid.

(*a*) *With Sulphuric Acid.*—When *o*-thiolbenzoic acid is heated in concentrated sulphuric acid with rather more than one molecular proportion of malonic acid, condensation occurs; but the products vary according to the temperature of the solution, the duration of the heating, and the strength of the acid employed. The most interesting, and, in this connexion, the most important of the products is "thioindigo," which may be readily prepared by this process. The *o*-thiolbenzoic acid (10 grams) was added to a solution of two molecular proportions of malonic acid in 150 c.c. of sulphuric acid, which contained about 20 per cent. of sulphur trioxide, the temperature of the liquid being maintained at about 75—80°. Immediate interaction took place with violent evolution of carbonic and sulphurous acids, the liquid assuming an intense green colour. When the effervescence had ceased, the liquid was poured over crushed ice, and the precipitated dye-stuff was then collected. By recrystallisation from xylene, "thioindigo" was obtained; it was identified (Found, $C=64{\cdot}7$. Calc., $C=65{\cdot}0$ per cent.) by its characteristic physical and chemical properties. In one experiment conducted in this manner the yield of "thioindigo" was about 80 per cent. of the theoretical, but in subsequent experiments this was not equalled, the product being then contaminated with an orange-brown substance, which, owing to its unsuitable character, has not been further investigated. By adopting lower temperatures (50—60°) during the condensation and by employing weaker sulphuric acid, this substance is obtained as the sole product, "thioindigo" being then absent. It may be added that at the higher temperatures of condensation a small quantity of "thioindigosulphonic acid" is usually formed.

(*b*) *Condensation with chlorosulphonic acid* proceeds more readily, and gives much better yields of "thioindigo" with greater certainty. The process is as follows: Very finely divided *o*-thiolbenzoic acid is gradually added to a cold mixture of rather more than the molecular proportion of malonic acid with chlorosulphonic acid. With each addition of thiolbenzoic acid a violent interaction occurs, carbonic and sulphurous acids being evolved. When all has been added and the interaction has subsided, the mixture is warmed to 45° for about two hours, and then poured over ice. "Thioindigosulphonic acid" is produced also by this method, but the yield of this product taken with the "thioindigo" is not far from the theoretical. The formation of the undesirable brown material has not been observed in this process.

Condensation of o-*Thiolbenzoic Acid with Ethyl Acetoacetate.*

The results of this interaction are more complex than those obtained with malonic acid; several different products may be isolated, and these usually occur together; but by varying the conditions, one or other may be made to predominate. While these experiments were in the initial stage, other work was published (Friedländer and Kielbasinski, *Ber.*, 1911, **44**, 3098) dealing with substances closely akin to those produced in this interaction, and, since the experiments from that source are apparently not yet complete, attention has been here confined to the simpler products.

It is shown in a subsequent paragraph that the formation of the compounds now described gives ample evidence for the purpose with which this investigation was undertaken.

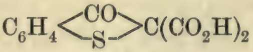
3-*Oxy*-(1)-*thionaphthen*.—Ten grams of *o*-thiolbenzoic acid and one and a-half times the equivalent proportion of ethyl acetoacetate were mixed with 150 c.c. of concentrated sulphuric acid, and the solution was warmed, the temperature being maintained at about 55°. Condensation proceeded with evolution of carbonic and sulphurous acids, and when this had ceased the product was poured over crushed ice. The precipitate was collected, and then treated with a current of steam, when the required substance accumulated in the distillate. The product, after being recrystallised from hot water, was identified as 3-oxy-(1)-thionaphthen by means of its characteristic physical and chemical properties. The yield was 5·5 grams, or about 55 per cent. of the theoretical. The condensation of the *o*-thiolbenzoic acid appears to be complete, and were it not for the formation of a considerable amount of red material during the distillation with steam, there is no doubt that the yields of the oxythionaphthen would be much greater. However, the method is very convenient for the preparation of small quantities of this substance in the laboratory. It is probable that the red substance is of similar nature to that recently obtained by Friedländer (*loc. cit.*) from the acid hydrolysis of 3-oxy-(1)-thionaphthen-2-aldehyde.

"Thioindigo" may be prepared from the reacting mixture described in the foregoing paragraph, but the heating must be prolonged after the first interaction has subsided, or a slightly higher temperature may be adopted to complete the oxidation of the oxythionaphthen to this dyestuff. Other substances, including the red material formerly mentioned, are then formed, and the yields of "thioindigo" are not good (3·5—4 grams), but experiments to improve this have not been made.

Finally, it may be mentioned that to ensure complete condensation of the *o*-thiolbenzoic acid it is necessary to employ this substance in a very fine state of division; otherwise some escapes interaction by caking together, the aggregates being attacked only on the surface.

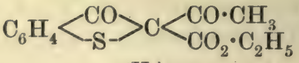
By employing in these experiments *o*-dithiobenzoic acid in place of *o*-thiolbenzoic acid, precisely similar results are obtained. The process then adopted was similar to that used with the latter acid, and a description is therefore unnecessary, but it may be remarked that the interaction of the dithio-acid is somewhat more sluggish that that of the mercaptan.

It is evident from the formation of the oxythiophen complex in these interactions that union is then effected between the *o*-thiobenzoic arrangement and the methylene group of malonic acid or of ethyl acetoacetate, the initial products of condensation being decomposed under the conditions, with loss of carboxyl (I) or of acetyl and carbethoxyl (II). It is necessary to remark that the



$$C_6H_4{<}^{CO}_{S}{>}C(CO_2H)_2$$

(I.)



$$C_6H_4{<}^{CO}_{S}{>}C{<}^{CO\cdot CH_3}_{CO_2\cdot C_2H_5}$$

(II.)

elimination of these groups in this manner is in harmony with previous experience, for it is well known that indoxyl-2-carboxylic acid is readily converted into indigo by concentrated sulphuric acid, and Friedländer (*Ber.*, 1911, **44**, 3100) has recently observed the removal of the aldehyde group from 3-oxy-(1)-thionaphthen-2-aldehyde by reaction with the diluted reagent. Other decompositions of similar nature have been recorded in the literature of patents.

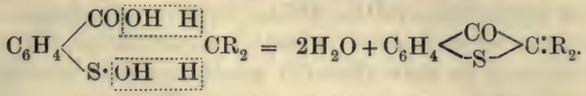
The condensation may be regarded as composed of two distinct processes which respectively involve the union of the thio- and carboxyl groups with the methylene; but the latter process does not here demand further attention, since it has been the subject of previous work on the production of "thioindigo." On the other hand, the direct union of the thiol group with methylene by means of sulphuric acid is a process of novel character, and a brief discussion of the mechanism involved may therefore not be out of place. The mode of formulating the interaction:

$$R\cdot SH+CH_2R_2+O=H_2O+RS\cdot CH_2R_2,$$

represents it as consisting of the simultaneous oxidation of the thiol and methylene groups, but for reasons similar to those previously advanced in discussing the production of thioxanthones from *o*-thiolbenzoic acid and aromatic substances (Davis and Smiles, Trans., 1910, **97**, 1290), the hypothesis cannot be here accepted as giving an adequate explanation. The insufficiency of the hypothesis is particularly evident when it is considered that the complex of oxythionaphthen is produced also from *o*-dithiobenzoic acid:

$$RS\cdot SR+2CH_2R_2+O_2=2RS\cdot CHR_2+2H_2O.$$

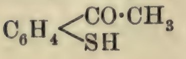
The facts collected in previous experiments have served to demonstrate (Trans., 1911, **99**, 640) that the sulphoxylic acids are formed in these mixtures of sulphuric acid with mercaptans or disulphides (according to i and ii, p. 570), and it has been shown that by considering the behaviour of these substances all the manifold reactions of mercaptans and disulphides in that solvent become correlated and simply explained. The novel reaction of these classes of compound which has been described in the foregoing pages is also brought into harmony with the others, for it is evident that the oxythionaphthen system is formed by direct condensation of the sulphoxylic acid with the methylene arrangement:



$$C_6H_4\left\langle\begin{matrix}CO\cdot OH\;\;H\\ S\cdot OH\;\;H\end{matrix}\right. CR_2 = 2H_2O + C_6H_4\left\langle\begin{matrix}CO\\ S\end{matrix}\right\rangle C{:}R_2.$$

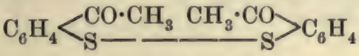
With regard to the question whether this interaction of a sulphoxylic acid and a methylene group is of general application, it may be remarked that the occurrence of the condensation depends to a great extent on the character of the thio-compound and of the methylene derivative, but the experiments made in this direction have been merely preliminary.

In conclusion, it is desirable to draw attention to the circumstance that there are many syntheses of compounds containing sulphur in a cyclic arrangement which probably depend on the intermediate formation of a sulphoxylic acid. This is especially remarkable when the interaction takes an abnormal course, which is otherwise inexplicable. One of the more interesting cases is a technical process (D.R.-P. 198,509) for the preparation of "thioindigo" by the oxidation of *o*-thiolacetophenone (I) or its derivatives by means of air in alkaline solution. The corresponding disulphide (II), which with fatty mercaptans or others of the aromatic series forms the normal and sole product of such oxidations, is here produced in relatively small amount, the greater portion of the product being the dyestuff, which is evidently formed from the oxythionaphthen (III) by further oxidation. It is clear that in this case the sulphoxylic acid (IV) which is at first formed



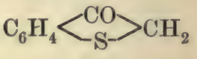
$$C_6H_4\left\langle\begin{matrix}CO\cdot CH_3\\ SH\end{matrix}\right.$$

(I.)



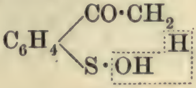
$$C_6H_4\left\langle\begin{matrix}CO\cdot CH_3\;\;CH_3\cdot CO\\ S\text{———————}S\end{matrix}\right\rangle C_6H_4$$

(II.)



$$C_6H_4\left\langle\begin{matrix}CO\\ S\end{matrix}\right\rangle CH_2$$

(III.)



$$C_6H_4\left\langle\begin{matrix}CO\cdot CH_2\\ \qquad\;\;\; H\\ S\cdot OH\end{matrix}\right.$$

(IV.)

by oxidation of the mercaptan, prefers to undergo the intramolecular rather than intermolecular condensation (as in ii, p. 570) leading to the disulphide (II). The same substance almost certainly plays a part in the production of "thioindigo" by another method, of which the mechanism has hitherto been obscure (P. Friedländer, "Jahrbuch der Chemie," R. Meyer, 1910, **20**, 466). The process in question (D.R.-P. 230641) consists of the interaction of sulphur chloride and acetophenone in the presence of chlorosulphonic acid. It is evident that the disulphide (II) is formed as a preliminary product, which in presence of the concentrated acid suffers hydrolytic fission (ii, p. 570) into the sulphoxylic acid

(IV), the latter reacting as already indicated. The yields of the dyestuff are stated to be poor, but this is not surprising, for extensive ortho-substitution of the dithio-group in acetophenone cannot be expected. Several other examples might be quoted, but those now given serve to show that the condensation of the sulphoxylic acids with aliphatic groups is possible, and is not confined to those containing the $\cdot CO\cdot CH_2\cdot CO\cdot$ arrangement, but under suitable conditions may also be effected with the acetyl group.

Summary.

Examples are given of the interaction of thiol and dithio-compounds with those containing the $\cdot CH_2\cdot CO\cdot$ group, the union of the thio- and methylene groups being effected by means of concentrated sulphuric acid or similar agents. The interaction is explained by the formation of a sulphoxylic acid. The examples given are taken from those which involve the formation of 3-oxy-(1)-thionaphthen.

In conclusion, we desire to express our thanks to Mr. W. G. Prescott for help afforded during the preliminary experiments.

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LXVI.—*Calcium Nitrate. Part I. The Two-component System: Calcium Nitrate–Water. Part II. The Three-component System: Calcium Nitrate–Nitric Acid–Water at* 25°.

By HENRY BASSETT, jun., and HUGH STOTT TAYLOR.

PART I.—*The Two-component System: Calcium Nitrate–Water.*

CALCIUM nitrate plays a sufficiently important part in the economy of nature to render its study both important and interesting.

It has long been known that the salt formed several hydrates, of which, however, only the highest, the tetrahydrate,

$$Ca(NO_3)_2,4H_2O,$$

has hitherto been well known. Millon (*Ann. Chim. Phys.*, 1842, [iii], **6**, 73) records the preparation of the tetrahydrate and a compound, $Ca(NO_3)_2,3\frac{1}{2}H_2O$. It was shown, however, by Gernez (*Ann. sci. Ecole Norm.*, 1878, [ii], **7**, 9) that the latter was in reality impure trihydrate, and that it crystallises from solutions containing less water than would correspond with $Ca(NO_3)_2,4H_2O$.

According to Marignac (*Ann. des Mines*, 1856, [v], **9**, 1), who examined the tetrahydrate crystallographically, it forms oblique, rhombic prisms belonging to the monoclinic system.

From vapour pressure measurements, Lescœur (*Ann. Chim. Phys.*, 1890, [vi], **21**, 511) deduced the existence of a di- and a tri-hydrate. Although the present investigation has shown that a dihydrate does exist, it is certain that it cannot be obtained by the method described by Lescœur, which can only yield mixtures of hydrates and the anhydrous salt.

The object of the following experiments was to examine the various solid phases which can separate from the two-component system, calcium nitrate–water, and to elucidate the conditions under which they may exist in contact with the saturated solution.

Calcium nitrate is a deliquescent and very soluble salt with a great tendency to form supersaturated solutions, in these respects showing a great similarity to calcium chloride. A few solubility determinations have been made at various isolated temperatures by Legrand (*Ann. Chim. Phys.*, 1835, [ii], **59**, 423), Mulder (*Scheikundige Verhandelingen en ond. Rotterdam*, 1864, **3**, 109), Guthrie (*Phil. Mag.*, 1876, [v], **2**, 211), Mylius and Funk (*Ber.*, 1897, **30**, 1718), Cameron and Robinson (*J. Physical Chem.*, 1907, **11**, 273). Most of the figures given show more or less divergence from the results tabulated below, the greatest differences being found in the earlier work, probably owing to insufficient attention having been given to constancy of the temperature and to complete saturation.

For the preparation of the solutions used in our experiments, pure recrystallised calcium nitrate was employed, the purity of which was checked by various qualitative tests. The stronger solutions were obtained by the use of a solution saturated at the boiling point or of the anhydrous salt, obtained from the tetrahydrate by dehydration at 150°. In all cases the solutions were tested to ensure their neutrality.

The solubilities, except those below −10°, were carried out in silica vessels, closed with rubber stoppers or with corks, carefully impregnated with paraffin wax. Except at the extreme limits, the regulation of the temperature was accurate to within 0·1°. The mixtures were shaken until several concordant values for the solubility had been obtained, the results recorded below representing the mean of these values. As a rule, where no change in the solid phase was needed, equilibrium, except in the more viscous solutions, was attained in from two to three days; in those cases where the original solid was not the correct stable phase, anything up to a month or even more was required. The solutions analysed were obtained by withdrawing a portion of the clear liquid by means of a pipette, special precautions being taken at the higher temperatures to prevent loss by evaporation.

The concentrations of the solutions were determined by estimating the total calcium as oxide, after precipitation as oxalate. Whenever possible the equilibrium solid was also analysed, but its separation in a state of purity presented some difficulty. This was more especially the case at the higher temperatures, or, in other words, with the more concentrated and viscous solutions. Owing to the ready solubility of calcium nitrate in alcohol, acetone, pyridine, etc., the solids could not be freed from solution by washing with such reagents. With the tetrahydrate, and in a less degree with the trihydrate, owing to the fair size of the crystals obtained, the solids could be obtained by filtration at the temperature of the experiment, followed by careful drying between filter paper, and then in a desiccator containing a quantity of the next higher hydrate or the anhydrous salt. In the case of the dihydrate the viscosity of the solutions prevented satisfactory separation of the solid phase, which was therefore not analysed. It was, however, certain that it was the dihydrate, as its crystallisation had been induced from supersaturated solutions, by inoculation with crystals of the dihydrate, of known purity, obtained as described in Part II (p. 585). With the anhydrous salt difficulties due to viscous solutions were also met, but owing to the higher temperatures were not quite so serious. Filtration by suction, and subsequent draining on porous plate, both at the temperature of the experiment, enabled solids to be separated containing upwards of 95 per cent. $Ca(NO_3)_2$. Even so, however, the characteristic crystalline form (cubical system) of the solid was ample confirmation of its anhydrous nature. Both the crystallised anhydrous salt and its dihydrate can only be conveniently prepared in a state of purity by the nitric acid method indicated in Part II.

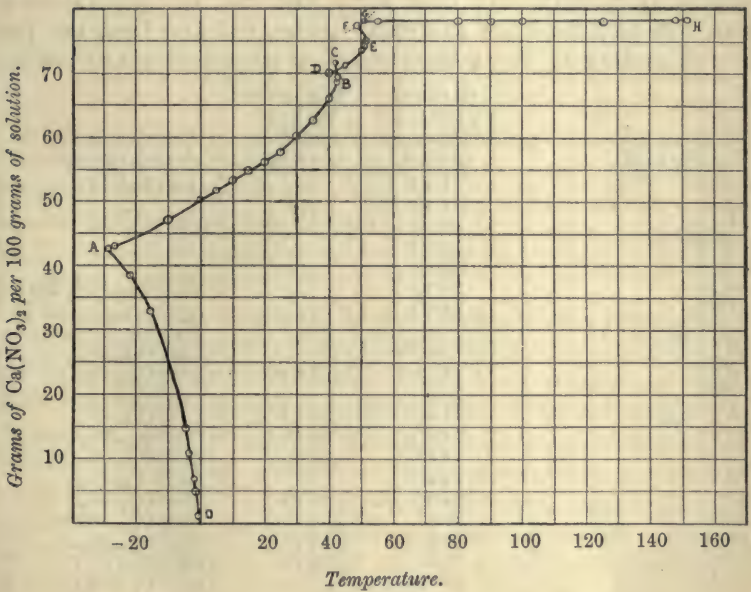
The equilibrium curves obtained by the study of the system are five in number, corresponding with the solid phases: ice; $Ca(NO_3)_2,4H_2O$; $Ca(NO_3)_2,3H_2O$; $Ca(NO_3)_2,2H_2O$; and $Ca(NO_3)_2$ respectively. They are plotted in Fig. 1.

Ice Curve and Cryohydric Point OA.—The freezing points of dilute solutions of calcium nitrate have already been determined by Arrhenius (*Zeitsch. physikal. Chem.*, 1888, **2**, 496), Rudorff (*Pogg. Ann.*, 1861, **114**, 63), and Raoult (*Zeitsch. physikal. Chem.*, 1888, **2**, 489), whilst more recently Jones and Getman (*Zeitsch. physikal. Chem.*, 1904, **49**, 403) have investigated more concentrated solutions. Only Rudorff's figures have been incorporated in our curve, as the others are not directly comparable, being expressed in gram mols. per litre. In obtaining the points on the ice curve, the solutions were agitated for several hours with the ice which had separated, the clear equilibrium solution being then separated and analysed, that is to say, the points were not mere freezing-point determinations, but true solubilities.

The cryohydric temperature was obtained by direct determination, and found to be −28·7°. The corresponding concentration, given by the point of intersection of the ice curve and the tetrahydrate curve, is 42·9 grams of $Ca(NO_3)_2$ per 100 grams of eutectic mixture.

FIG. 1.

Two-component system : Calcium nitrate–Water.



Tetrahydrate Curve ABC.—The tetrahydrate possesses a true melting point, and its solubility curve has the form characteristic of such cases.

The melting point was determined, both by direct observation and by means of a time-temperature cooling curve, using a carefully prepared specimen of the salt. The temperature thus found was 42·7°.

Trihydrate Curve DEF.—The trihydrate was originally obtained by allowing a supersaturated solution to crystallise at about 45°; solubility determinations were carried out between the limits of 40° and 51°. This hydrate also has a true melting point at 51·1°, obtained in the manner indicated above.

Dihydrate Curve FG.—Solutions in stable equilibrium with the dihydrate can only exist between the limits of temperature 48·4° and 51·3°. That this hydrate can possess no true melting point in the stable region is at once evident from a study of its composition and the course of its anhydrous curve.

Curve of the Anhydrous Salt GH.—Above 51·3° the anhydrous salt is the stable solid phase. The curve is almost parallel to the temperature axis, showing a slight upward trend. That a slight increase in concentration does occur with rise of temperature is clear, not only from the analytical figures, but also from the fact that on cooling to 55° a clear solution saturated at 140°; small

Temperature.	Grams of $Ca(NO_3)_2$ per 100 grams of solution.	Analysis of the solid phase CaO, per cent.	Composition of the solid phase.
−0·4°	1·40	Nil.	Ice (Rudorff)
−1·4	4·78	,,	,, ,,
−1·9	6·53	,,	,, ,,
−3·05	10·00	,,	,, ,,
−4·15	12·98	,,	,, ,,
−15·70	33·13	,,	Ice (Bassett & Taylor)
−21·70	38·70	,,	,, ,, ,,
−28·70 (Cryo. Pt.)	—	—	Eutectic mixture
−26·70	43·37	—	$Ca(NO_3)_2,4H_2O$
−10·00	47·31	23·64	$Ca(NO_3)_2,4H_2O$
0·0	50·50	—	$Ca(NO_3)_2,4H_2O$
5·0	51·97	23·80	$Ca(NO_3)_2,4H_2O$
10·0	53·55	24·18	$Ca(NO_3)_2,4H_2O$
15·0	54·94	23·80	$Ca(NO_3)_2,4H_2O$
20·0	56·39	—	$Ca(NO_3)_2,4H_2O$
25·0	57·98	24·18	$Ca(NO_3)_2,4H_2O$
30·0	60·41	—	$Ca(NO_3)_2,4H_2O$
35·0	62·88	23·93	$Ca(NO_3)_2,4H_2O$
40·0	66·21	24·07	$Ca(NO_3)_2,4H_2O$
42·4	68·68	—	$Ca(NO_3)_2,4H_2O$
42·5	68·74	—	$Ca(NO_3)_2,4H_2O$
42·7 (m. p. of $-4H_2O$)	—	—	$Ca(NO_3)_2,4H_2O$
42·45	71·70	—	$Ca(NO_3)_2,4H_2O$
40·0	70·37	25·80	$Ca(NO_3)_2,3H_2O$
45·0	71·45	25·80	$Ca(NO_3)_2,3H_2O$
50·0	73·79	25·94	$Ca(NO_3)_2,3H_2O$
51·0	74·73	—	$Ca(NO_3)_2,3H_2O$
51·1 (m. p. of $-3H_2O$)	—	—	$Ca(NO_3)_2,3H_2O$
49·0	77·49	—	$Ca(NO_3)_2,2H_2O$
51·0	78·05	—	$Ca(NO_3)_2,2H_2O$
55·0	78·16	32·24	$Ca(NO_3)_2$
80·0	78·20	—	$Ca(NO_3)_2$
90·0	78·37	33·76	$Ca(NO_3)_2$
100·0	78·43	32·91	$Ca(NO_3)_2$
125·0	78·57	—	$Ca(NO_3)_2$
147·5	78·80	—	$Ca(NO_3)_2$
151·0	79·00	33·39	$Ca(NO_3)_2$

quantities of the characteristically crystalline anhydrous salt separate.

The saturated solution was found to boil at 151°/760 mm., and contained 79 grams of $Ca(NO_3)_2$ per 100 grams of solution.

The data given on p. 580 are entirely solubility data. With a view to the more accurate determination of the curves in the neighbourhood of the two melting points, *B* and *E*, a number of freezing-point measurements were carried out, using the technique employed by Lidbury (*Zeitsch. physikal. Chem.*, 1902, **39**, 453). Anomalous results have been obtained, which cannot as yet be satisfactorily explained, and for the elucidation of which further experimental work is being undertaken.

PART II.—*The Three-component System: Calcium Nitrate–Nitric Acid–Water at* 25°.

In the investigation of the aqueous solubilities of calcium nitrate there was no difficulty in investigating either the anhydrous calcium nitrate or its tri- and tetra-hydrates, owing to the relatively large range of temperature over which they were the stable solid phases, and, in the case of the two hydrates, to the fact that they possessed true melting points.

In the case of the dihydrate, however, matters were not so simple, for, in the first place, its range of stable existence is only 2·9°, and secondly, the solutions with which it can be in equilibrium are so concentrated and therefore so viscous that it is not possible to separate any of the crystals for analysis in such a state of freedom from adhering mother liquor that the analytical figures obtained can be relied upon to definitely decide between, say, a di- or a mono-hydrate. For the same reasons it was not possible to prove, from an investigation of the pure aqueous solutions alone, whether $Ca(NO_3)_2,2H_2O$ was the only hydrate intermediate between the anhydrous salt and its trihydrate, or whether there might not be a monohydrate as well, stable over a very short temperature range.

In order to settle these various points, the solubility of calcium nitrate in nitric acid of different concentrations has been investigated at 25°.

It has been found, as was to be expected, that the addition of nitric acid considerably diminishes the solubility of the calcium nitrate, whilst the solid phase undergoes in succession a number of changes identical with those produced by rise of temperature in the pure aqueous solutions. As the concentration of the acid is increased, the tetra-, tri-, and di-hydrates and the anhydrous salt become the stable solid phases in equilibrium.

The solubility determinations were carried out in silica flasks, closed with corks impregnated with paraffin wax at low concentrations of nitric acid, and with stoppers of cerasin wax where the concentration of nitric acid was sufficiently high to cause decomposition of the cork by the acid fumes. The bottles were placed in a large thermostat carefully regulated to 25°, and were shaken several times a day. The decreased efficiency caused by the non-rotation of the solutions and solids in the thermostat was compensated for by the length of time allowed for equilibrium to be attained. In all cases the results given represent the mean of two concordant analyses, the latter of which was effected upwards of a week after the former with the solutions remaining over from the first determination. In this manner absolute saturation of the solvent was ensured.

The statement made in Part I. with regard to the time required for equilibrium to be reached applies equally well to the present case.

In all the solubility determinations both the solution and the solid in equilibrium were analysed. In the case of the solutions the total lime and the free nitric acid were determined in a weighed quantity, the former as CaO after precipitation as oxalate, and the nitric acid by titration with *N*/10-sodium carbonate.

For the determination of the composition of the solid phases, it was found most convenient to free the crystals as far as possible from adhering solution by suction. They were then dried between blotting paper and allowed to remain on porous plate for about half-an-hour in a desiccator containing solid potassium hydroxide and concentrated sulphuric acid. As in most cases the crystals were of fair size, this method gave results of accuracy sufficient to identify the solid phase with absolute certainty. The solids were always tested, however, for free acid. In most of the determinations traces of acid were found, probably sometimes enclosed within the larger crystals.

The solubilities obtained and the composition of the solid phases in equilibrium are collected in the following table:

	100 grams of solution contain			
Materials employed for the solution.	$Ca(NO_3)_2$, grams.	HNO_3, grams.	Solid phase contains CaO, per cent.	Composition of solid phase.
$Ca(NO_3)_2,4H_2O$ and water	57·98	nil	24·18	$Ca(NO_3)_2,4H_2O$
$Ca(NO_3)_2,4H_2O,HNO_3,H_2O$ ...	54·82	3·33	23·76	$Ca(NO_3)_2,4H_2O$
	52·96	5·87	24·01	$Ca(NO_3)_2,4H_2O$
	51·58	7·21	23·88	$Ca(NO_3)_2,4H_2O$
	47·82	11·27	23·95	$Ca(NO_3)_2,4H_2O$
	45·59	13·71	24·08	$Ca(NO_3)_2,4H_2O$
	40·70	19·65	24·01	$Ca(NO_3)_2,4H_2O$

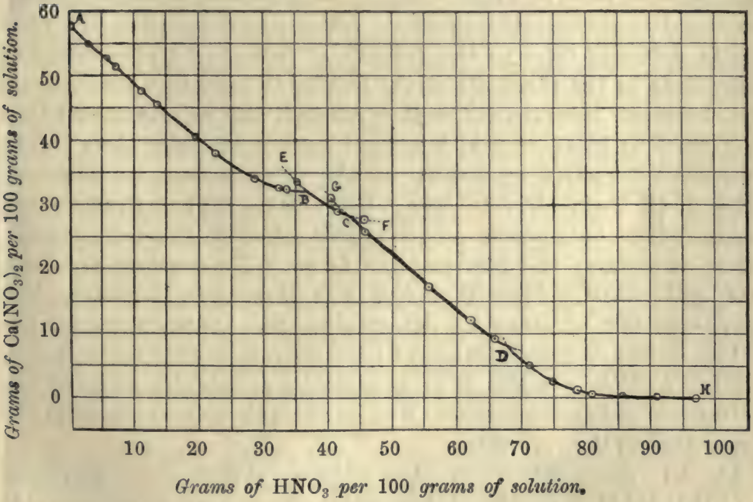
Materials employed for the solution.	100 grams of solution contain $Ca(NO_3)_2$, grams.	100 grams of solution contain HNO_3, grams.	Solid phase contains CaO, per cent.	Composition of solid phase.
$Ca(NO_3)_2,4H_2O,HNO_3,H_2O$ …	38·17	22·80	24·05	$Ca(NO_3)_2,4H_2O$
	34·46	28·81	—	$Ca(NO_3)_2,4H_2O$
$Ca(NO_3)_2,4H_2O + HNO_3$ conc. …	32·84	32·63	24·36	$Ca(NO_3)_2,4H_2O$
	32·50	33·52	—	$Ca(NO_3)_2,4H_2O$
$Ca(NO_3)_2,3H_2O + HNO_3 + H_2O$ ..	33·44	35·63	26·12	$Ca(NO_3)_2,3H_2O$*
	29·05	41·66	25·38	$Ca(NO_3)_2,3H_2O$
	27·79	45·70	25·80	$Ca(NO_3)_2,3H_2O$*
$Ca(NO_3)_2 + HNO_3 + H_2O$ ………	31·09	40·56	27·18	$Ca(NO_3)_2,2H_2O$*
	26·07	45·70	28·20	$Ca(NO_3)_2,2H_2O$
$Ca(NO_3)_2, HNO_3$ conc. …………	17·41	55·48	26·90	$Ca(NO_3)_2,2H_2O$
	12·25	62·05	28·05	$Ca(NO_3)_2,2H_2O$
	9·34	65·69	28·15	$Ca(NO_3)_2,2H_2O$
	8·52	67·20	28·10	$Ca(NO_3)_2,2H_2O$
$Ca(NO_3)_2 + HNO_3$ conc. $+ HNO_3$ anhyd.	5·06	71·12	33·67	$Ca(NO_3)_2$
	2·53	74·77	34·05	$Ca(NO_3)_2$
	1·05	78·56	—	$Ca(NO_3)_2$
	0·54	80·83	33·88	$Ca(NO_3)_2$
	0·36	85·83	34·10	$Ca(NO_3)_2$
	0·01 about	90·90	—	$Ca(NO_3)_2$
	nil	96·86	—	$Ca(NO_3)_2$

The results tabulated above are set forth in Fig. 2. The portion *AB* of the curve indicates solutions in equilibrium with $Ca(NO_3)_2,4H_2O$. Point *A* represents the aqueous solution in equilibrium with this hydrate. Point *B* [$Ca(NO_3)_2 = 32·0$ grams;

FIG. 2.

Three-component system: Calcium nitrate–Nitric acid–Water.

Isothermal at 25°.



$HNO_3 = 37$ grams per 100 grams of solution] indicates the concentration at which both solid tetrahydrate and solid trihydrate can co-exist in contact with the saturated acid solution. The trihydrate has only a short range of existence as the stable form, namely, between the limits 37 and 43 grams of nitric acid, indicated on the diagram by the curve *BC*. Two solubilities on the unstable branches of the curve, *BE* and *CF*, have, however, been obtained, and are indicated in the table by an asterisk in the last column. Point *C* [$Ca(NO_3)_2 = 28{\cdot}7$ grams; $HNO_3 = 43$ grams per 100 grams of solution] represents the concentration at which trihydrate and dihydrate can co-exist with the saturated solution. The curve *CD*, with the extension *CG* into the unstable region, indicates the composition of saturated solutions in equilibrium with the dihydrate. Point *D* represents the composition of the solution at which dihydrate and the anhydrous salt can co-exist in contact with the saturated solution, whilst *DH* represents the composition of solutions in equilibrium with the anhydrous salt.

The tetrahydrate, as was observed by Marignac (*Ann. des Mines*, 1856, [v], **9**, 28) and Millon (*Compt. rend.*, 1842, **14**, 905), crystallises in monoclinic prisms. These have usually a considerable length in proportion to their breadth, and are generally well developed. The trihydrate crystallises in flattened, prismatic forms, which appear to belong to the triclinic system. The crystals are usually about three times as long as they are broad, and may reach a centimetre or more in length. The crystals formed by the dihydrate are usually considerably smaller. They are prismatic, but of a totally different type to the crystals of tetra- or tri-hydrate, the dimensions in the three directions not being very dissimilar. As a rule, however, they are not well developed, and so intergrown that it is hard to know to which crystal system to refer them. The anhydrous $Ca(NO_3)_2$ crystallises in the cubic system, as shown by Retgers (*Zeitsch. Kryst. Min.*, 1889, **21**, 257). Preparations obtained from hot aqueous or nitric acid solutions generally contain cubes, octahedra, and intermediate forms. The crystals are, as a rule, quite small, seldom exceeding a millimetre in diameter. The anhydrous salt obtained by dehydrating the hydrated compounds at 150° forms irregular grains without definite crystalline form.

With a little practice it is possible to distinguish each of the hydrates of calcium nitrate, as well as the anhydrous salt, from the appearance of the crystals.

As an examination of the figure shows, the dihydrate $Ca(NO_3)_2,2H_2O$ was the stable solid phase over a considerable range of nitric acid concentration, and, moreover, the equilibrium solutions contained relatively little calcium nitrate. Both these facts much facilitated the study of the dihydrate. The latter by suitable manipulation could be obtained in crystals of a moderate size, from which the relatively mobile equilibrium solution could be separated almost entirely; in fact, the dihydrate was first obtained in this way, and used for seeding out those of the pure aqueous solutions supersaturated with respect to it. As the diagram and the tabulated figures show, there is a transition from the dihydrate to the anhydrous salt at a concentration of about 67·5 per cent. of nitric acid without any indications of the existence of a monohydrate.

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LXVII.—*The Behaviour of Alloys when Heated in a Vacuum.*

By CLARENCE RICHARD GROVES and THOMAS TURNER.

THE introduction of the electric resistance tube furnace in its various modifications has provided the experimenter with a ready means of obtaining a uniform and easily regulated high temperature combined with varying pressures. Advantage has been taken of this form of apparatus to determine the boiling points of metals, to study the solubility of gases in metals, to examine the cause of "growth" in cast iron, and to conduct further investigations which would otherwise have been difficult or almost impossible. In a recent paper (T. Turner, "On the behaviour of certain alloys when heated *in vacuo*," *Institute of Metals*, January, 1912) one of us has described some experiments conducted in this form of furnace, and shown that when brass is heated in a vacuum to the melting point of copper, the zinc is quantitatively removed and the copper obtained in the metallic state. Similarly, if an alloy containing zinc and iron is heated in a vacuum, the two metals can be readily and completely separated provided that a proper temperature is employed. Below about 500° the separation is slow, at 600° a little iron volatilises with the zinc, but at about 500° the separation is complete. It had already been shown by Tiede and Fischer (*Ber.*, 1911, **44**, 1712) that lead could be separated from tin by heating in a vacuum, although the proper temperature does not appear to have been recorded. By heating gold with an excess of cadmium in an exhausted hard glass tube with a gas burner, Heycock and Neville (Trans., 1892, **41**, 914) had obtained the compound AuCd, whilst Berry (*Proc. Roy. Soc.*, 1911, *A*, **86**, 67) has succeeded in isolating the compound $MgZn_2$ by distillation in a vacuum.

The experiments now to be described may be regarded as a continuation of those recently communicated to the Institute of Metals. The alloys examined, except where otherwise stated, were prepared by melting together suitable proportions of the purest metals commercially obtainable, such as electrolytic copper, "Mond" zinc, assay lead, Cookson's specially selected antimony, etc. In each case the composition of the resulting alloy was checked by the direct determination of the chief constituent. In the majority of instances binary alloys were employed, and in cases where the direct determination of the second constituent was inconvenient, it was estimated by difference. Weighed quantities of the alloys were placed in a porcelain boat, and heated in a porcelain tube in an electric resistance tube furnace. The temperatures were observed by means of a Le Chatelier thermocouple. As the couple wires would have been attacked by the volatile metal if the couple were placed inside the experimental tube, it was found necessary to insert the couple between the inner and outer tubes of the furnace. As the heating is slow, usually taking about one hour, and the actual experiment lasted from half an hour to two hours, it is probable that the difference in temperature between the inside and outside of the experimental tube was small. The ends of the tube extended some 10—20 cm. out of the furnace, and so were always cool. At one end of the experimental tube a glass plate was sealed on with sealing wax, and the boat could thus be readily viewed when the temperatures employed exceeded about 600°. At the other end of the tube a glass reduction piece, also sealed with sealing wax, was connected with a phosphoric oxide drying tube, a shortened mercury pressure gauge, and a simple mercury pump on the Töpler principle. The apparatus was exhausted until the pressure was less than 1 mm. All the joints, except the two above mentioned, were of glass, and no rubber or grease was employed. There was no appreciable fall of pressure when the apparatus was exhausted overnight and used next morning.

The range of temperature employed extended from about 350° to 1200°. This was selected because it represents the temperatures actually employed in melting the alloys on the commercial scale. There is also the further consideration that 1200° very nearly approaches the limit for repeated safe heatings with a platinum wound furnace, and the point at which a porcelain tube ceases to be gas-tight. Within the range of temperature and time employed, it was found that when alloys are heated in a vacuum their behaviour is such as permits of a classification into five groups, as follows:

Group I.—The metals are non-volatile, and the alloy is unaltered in weight.

Group II.—The volatile metal or metals are completely removed, and a quantitative separation results.

Group III.—Any excess of volatile metal is removed, and a chemical compound remains.

Group IV.—Any excess of volatile metal is removed, but the residue is not a chemical compound.

Group V.—The metals composing the alloy volatilise together, their relative proportions being, in part, dependent on the temperature employed.

Although in the above classification certain metals are stated to be non-volatile, this description must, of course, be regarded as relative rather than absolute. Presumably there is some vapour tension with every metal, even at the ordinary temperature. By sufficiently long and careful observation, Demarçay detected the volatility of zinc in a vacuum at 184°. Copper, nickel, and other metals of similar character are therefore doubtless appreciably volatile at 1200°. The loss of weight is, however, within the limits of ordinary experimental error during a period not exceeding two hours.

EXPERIMENTAL.

I.—*Alloys of the First Group: Non-volatile at* 1200°.

(*a*) *Copper–Aluminium Series.*—The alloy employed was prepared by Mr. J. H. Chamberlain in connexion with a research on the volume changes in the Cu–Al series. On analysis it yielded Cu = 32·60 per cent. Of this alloy 0·5 gram was heated in a vacuum at 1100° for thirty minutes. The residue weighed 0·4995 gram, and the loss was 0·10 per cent., which may be regarded as being within the limit of experimental error. Hence neither metal was appreciably volatilised.

(*b*) *Copper–Nickel Series.*—The alloy used was a selected commercial cupro-nickel, and contained as nearly as possible Cu = 80 per cent. One gram of the alloy was heated in a vacuum at 1200° for thirty minutes. The residue in the boat weighed 1·0002 grams; hence neither metal was volatile.

(*c*) *Copper–Tin Series.*—An alloy was prepared by melting together four parts of copper and one part of tin. In this case the resulting composition was not checked by analysis.

One gram of this alloy was heated in a vacuum for thirty minutes at 1100°. The residue weighed 0·9998 gram, so that no appreciable loss of weight occurred.

(*d*) *Copper–Iron Series.*—In the paper read before the Institute of Metals it was shown that when a complex copper alloy was heated in a vacuum to 1200°, the zinc and lead volatilised, but the iron remained behind with the tin and copper. There is little doubt, therefore, that the Cu–Fe series belongs to this group of alloys.

II.—*Alloys of the Second Group: Quantitatively Separable.*

(*a*) *Copper–Bismuth Series.*—An alloy was prepared of approximately 75 per cent. of copper and 25 per cent. of bismuth. On analysis it yielded Cu = 74·40 per cent. One gram of the alloy was heated in a vacuum for thirty minutes at 1100°. The residue weighed 0·7440 gram, which corresponded exactly with the proportion of copper present. On applying the lead iodide colour test for bismuth to this residue, only a very minute trace of bismuth was detected. The bismuth was therefore completely volatilised.

(*b*) *Copper–Lead Series.*—In a similar manner a 75:25 copper–lead alloy was prepared. On analysis it yielded Cu = 74·60; Pb = 25·32 per cent. Two grams of the alloy were heated in a vacuum for forty-five minutes at 1100°, and the residue weighed 1·4902 grams, or 74·51 per cent. This copper was tested for lead, but the quantity remaining was too small to be estimated.

(*c*) *Copper–Zinc Series.*—In the former paper (*loc. cit.*) it was shown that two samples of brass containing by analysis 36·90 and 28·63 per cent. of zinc respectively, lost in a vacuum at 1200°, the first 36·80 per cent., and the second 28·85 per cent. Hence the whole of the zinc was volatilised.

These observations have been confirmed by the examination of an alloy prepared from pure materials for another purpose. It contained exactly 70 per cent. of copper and 30 per cent. of zinc. Five grams of this brass when heated in a vacuum for thirty minutes at 1100° left a residue of metallic copper, which weighed 3·5029 grams, or 70·06 per cent. of the original alloy. It was carefully tested for zinc with negative results.

(*d*) *Iron–Zinc Series.*—In the former paper (*loc. cit.*) particulars were given of the result of the heating in a vacuum of "hard zinc," an alloy containing 4·71 per cent. of iron, 0·81 per cent. of lead, and the remainder zinc. It was shown that at 1000° more than half of the iron which was present volatilised with the zinc and lead; as the temperature fell, the proportion of iron which volatilised became less and less, until at 500° pure iron was left as a residue, whilst the whole of the zinc volatilised, and was then free from iron. Iron and zinc are thus completely separable at about 500°.

(*e*) *Lead–Tin Series.*—Tiede and Fischer have found, as already mentioned in the earlier part of this paper, that tin can be quantitatively separated from lead by heating in a vacuum, but details as to temperatures are lacking.

III.—*Alloys of the Third Group: Yielding a compound.*

(*a*) *Gold–Zinc Series.*—An alloy was prepared containing about one-sixth of its weight of gold, and the remainder zinc, the object being approximately to reproduce the composition of the gold–zinc residues obtained in the cyanide method of extraction of gold from its ores. The alloy on analysis gave Au = 17·41 per cent. Of this alloy 0·5 gram was heated in a vacuum at 500° for thirty minutes. The residue weighed 0·1128 gram, and contained 0·0852 gram of gold. The composition of the residue was therefore Au = 75·50; Zn = 24·50 per cent.

A duplicate experiment, in which the length of heating was increased to ninety minutes, gave almost identical results. The compound AuZn is known, and requires Au = 75·1 per cent.

(*b*) *Copper–Antimony Series.*—An alloy was prepared from three parts of copper and one part of antimony. On analysis it yielded Cu = 74·70 per cent. Of this alloy 1 gram was heated at 1100° for thirty minutes. The residue weighed 0·9900 gram, and the slight loss was probably due to spitting, which is not unfrequently observed when copper alloys are melted in a vacuum. The experiment suggested either that antimony was non-volatile, or that a definite compound was formed.

In order further to test the matter, an alloy richer in antimony was prepared. On analysis this gave Cu = 25·20; Sb = 74·60. Total = 99·80 per cent. One gram of this alloy was heated in a vacuum at 1100° for thirty minutes, and yielded a residue which weighed 0·4120 gram. Hence 0·588 gram of antimony had been volatilised. The residue was white and crystalline, and yielded on analysis Cu = 61·26; Sb = 38·56. Total = 99·82 per cent. This composition gives an atomic ratio which is almost exactly that of Cu_3Sb, which is therefore evidently stable in a vacuum at 1100°. A repetition of the experiment gave similar results.

(*c*) *Gold–Cadmium Series.*—As already stated, Heycock and Neville have obtained the definite compound AuCd by heating gold with excess of cadmium in an exhausted hard glass tube, one end of which was bent over and cooled.

(*d*) *Magnesium–Zinc Series.*—The compound $MgZn_2$ has been obtained by Berry (*loc. cit.*) by heating the metals in a vacuum.

IV.—*Alloys of the Fourth Group: Residue retains some volatile metal in solution.*

(*a*) *Copper–Arsenic Series.*—An alloy was made from approximately equal quantities of arsenic and copper. It yielded on analysis Cu = 50·95; As = 49·00. Total = 99·95 per cent. Of this alloy 1 gram was heated in a vacuum at 1100° for thirty minutes. The residue weighed 0·6318 gram, so that 0·3682 gram of arsenic was lost by volatilisation. This residue yielded on analysis Cu = 80·60; As = 19·40 per cent. As this composition does not correspond with any simple atomic proportion, the experiment was repeated, but the time of heating increased to two hours. The residue from 1 gram weighed 0·6236 gram, and its composition was Cu = 80·50; As = 19·50 per cent. The proportion of arsenic appears, therefore, to be fixed, whether the time of heating be long or short.

A microscopical examination of the metallic residue, after polishing and etching with dilute ammonia, showed the presence of two constituents, one being areas of a white colour, and the other a blue network. The known compound richest in arsenic is Cu_3As. At high temperatures it would appear that a stable solution of this compound exists in copper containing arsenic, and that on cooling a separation into two constituents takes place.

V.—*Alloys of the Fifth Class: Two (or more) metals volatilise together.*

(*a*) *Silver–Zinc Series.*—This series is of special interest because of the large quantities of silver–zinc scum which are produced in the Parkes' lead desilverising process. An alloy was prepared from equal weights of silver and zinc, which gave on analysis: Ag = 50·46; Zn = 49·64. Total = 100·10 per cent.

Experiments were conducted in order to ascertain the best temperature for separating zinc and silver in a vacuum. In each case 1 gram of the alloy was taken, and the results obtained are given in the following table. The silver used in each experiment was 0·5046 gram.

Temperature.	Time in minutes.	Weight of residue.	Silver in residue.	Zinc in residue.	Percentage composition of residue.	
					Silver.	Zinc.
500°	45	0·7582	0·4994	0·2588	65·86	34·14
500	120	0·7350	0·5038	0·2312	68·46	31·54
600	120	0·6052	0·5040	0·1012	83·28	16·72
700	120	0·5104	0·5038	0·0066	98·68	1·32
1000	30	0·4924	0·4892	0·0033	99·33	0·67

It will be seen that as the time increases the zinc gradually passes off at lower temperatures, or more quickly in similar times as the temperature rises. The residue obtained at 600° contained 83·28 per cent. of silver, as compared with 83·29 required for Ag_3Zn. It is possible that further tests would indicate that this compound is stable at 600°, but decomposed at a rather higher temperature. At present the existence of such a compound must be regarded as not proved. For commercial purposes a separation might be effected at 600°, as the residue would only retain one part of zinc to five of silver, and such bullion could then be refined after the bulk of the zinc had been recovered.

At temperatures necessary to remove the last portions of the zinc an appreciable loss of silver occurs, as zinc and silver then tend to pass over together.

(*b*) *Silver–Lead Series.*—An alloy intended to contain about equal weights of lead and silver was prepared; on analysis it yielded Ag = 49·60; Pb = 50·31. Total = 99·91 per cent.

Of this alloy 1 gram was heated in a vacuum at 1000° for two hours. The residue weighed 0·4578 gram, so that 0·5422 gram volatilised. This residue contained 0·4548 gram of silver; 3·82 per cent. of silver had volatilised with the lead, whilst 0·3 per cent. of lead remained with the silver. In other words, one-fourteenth of the silver had been lost before the whole of the lead was removed.

(*c*) *Lead–Zinc Series.*—In the previous paper (*loc. cit.*) it has been shown that from a complex alloy consisting chiefly of copper, 7·11 per cent. of lead and 11·65 per cent. of zinc were completely removed and volatilised together, when the alloy was heated in a vacuum to 1200°. Other tests show that lead and zinc readily pass away together when heated in a vacuum.

In conclusion, it may be pointed out that any series of experiments such as those above described can obviously only be regarded as a preliminary investigation. An innumerable list of alloys invites further inquiry. Hitherto the experiments have been almost entirely confined to the simplest case, in which one part of the apparatus is cold, and the vapour pressure inside the experimental tube almost zero. The conditions which would arise with variations in the pressure of the metallic vapours, or of the pressure of other gases, present problems which can only be solved by a number of skilled and patient workers.

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LXVIII.—*Electro-reduction of Alkylnitrosoamides.*

By Hilmar Johannes Backer.

Whilst the reduction of the dialkylnitrosoamines led to the discovery of the aliphatic hydrazines, the reduction of nitrosoamides has often been attempted unsuccessfully. Only the alkylnitrosocarbamides and alkylnitrosourethanes, which to some extent may be considered as nitrosoamides, have been reduced to hydrazine derivatives (E. Fischer, *Annalen*, 1879, **199**, 288; v. Brüning, *ibid.*, 1889, **253**, 7; Klobbie, *Rec. trav. chim.*, 1890, **9**, 148; Backer, *Diss.*, Leyden, 1911, 190, 197).

The alkylnitrosoamides of common organic acids, however, never yielded the corresponding hydrazides. The attempts by O. Fischer (*Ber.*, 1876, **9**, 464; 1877, **10**, 960), Wohl (*Ber.*, 1892, **25**, 3632), v. Pechmann and Frobenius (*Ber.*, 1894, **27**, 652), Willstätter and Stoll (*Ber.*, 1909, **42**, 4872) either resulted in a loss of the nitroso-group, or quite a different reaction took place.

With the view of attempting the reduction in a simple case, *s*-dimethyloxamide was nitrosated. The *oxalylbismethylnitrosoamide* obtained is very sensitive to inorganic acids, and is immediately decomposed by bases. Being also very unstable by itself, it forms a remarkable contrast to the corresponding nitroamide, which may be kept for years without any perceptible alteration.

Owing to this instability, reduction by zinc dust and acetic acid did not succeed. The delicate electrochemical method was therefore attempted, by which sensitive nitroamino-compounds are readily reduced to hydrazines, that is, electro-reduction in slightly acid solution with a tinned cathode (*Rec. trav. chim.*, 1912, **31**, 1).

By this method the corresponding hydrazide was indeed obtained, although only to a small amount. It was isolated by condensation with benzaldehyde.

The above-mentioned decomposition of the nitrosoamide by bases was further investigated, and was found to be quite analogous to the reaction observed by v. Pechmann (*Ber.*, 1894, **27**, 1888; 1895, **28**, 855) with methylnitrosourethane. Potassium hydroxide, for example, yields diazomethane * and potassium oxalate:

$$\cdot CO\cdot N(NO)\cdot CH_3 + KOH = \cdot CO\cdot OK + HN(NO)\cdot CH_3 \longrightarrow N\vdots N\dot{:}CH_2.$$

---

* Although this reaction proceeds most readily, it is not well adapted for preparing diazomethane, because the nitrosoamide has to be freshly prepared for each occasion. Von Pechmann's method or the new method of Staudinger and Kupfer (*Ber.*, 1912, **45**, 505) is therefore preferable.

The decomposition by ammonia which is said to take place in quite a different way (v. Pechmann, *Ber.*, 1894, **27**, 1888) was found to be similar, oxamide and diazomethane being formed:

$$\cdot CO\cdot N(NO)\cdot CH_3 + NH_3 = \cdot CO\cdot NH_2 + HN(NO)\cdot CH_3 \longrightarrow N{:}N{:}CH_2.$$

Ammonia derivatives, such as amines and hydrazines, act in the same way.

When the reaction proceeds slowly, the diazomethane formed is partly decomposed, with evolution of nitrogen and possible methylation of the excess of amine.

The other reaction product is always the oxalyl derivative of the amine or hydrazine. Possibly the nitrosoamide might be employed for the introduction of the oxalyl group when oxalyl chloride cannot be used.

Willstätter and Stoll (*Ber.*, 1909, **42**, 4872) observed an analogous decomposition of aromatic nitrosoamides by phenylhydrazine, and applied the same reaction to methylnitrosourethane, without mentioning, however, the formation of diazomethane. Recently Haager (*Monatsh.*, 1911, **32**, 1089) investigated a similar reaction with phenylnitrosocarbamide and aromatic amines.*

In order to test the reduction and decomposition on a second example of the same kind, *succinylbismethylnitrosoamide* was prepared. Its properties are similar to those of the oxalic derivative, but it is more stable, and its reaction with various bases is much slower.

Electro-reduction furnished the corresponding hydrazide, which was separated by condensation with benzaldehyde.

EXPERIMENTAL.

I.—*Oxalylbismethylnitrosoamide*, $NO\cdot NMe\cdot CO\cdot CO\cdot NMe\cdot NO$.

Preparation.—The nitrosation of *s*-dimethyloxamide cannot be effected by the usual method (sodium nitrite and hydrochloric acid), but succeeds most easily when its acetic acid solution is treated with nitrous anhydride. Five grams of *s*-dimethyloxamide are suspended in 30 c.c. of glacial acetic acid, which dissolves the greater part. A fairly rapid current of nitrous anhydride (from arsenious oxide and nitric acid, D 1·35) is passed through the liquid, which is cooled with water, for fifteen or twenty minutes, until a dark green solution is obtained. On diluting with the

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* Instead of the three explanations given by Haager (*loc. cit.*, 1095, 1097), it seems far more likely that the reaction is a double decomposition of the same kind as those described in the present paper:

$$PhN(NO)\cdot CO\cdot NH_2 + PhNH_2 = PhN{:}NOH + PhNH\cdot CO\cdot NH_2.$$

The diazobenzene may then, with the remaining aniline, yield diazoaminobenzene.

double volume of ice-water, the nitroso-compound at once separates as a rapidly crystallising oil. The product is collected without delay, washed with water until free from acid, and then dried by pressing between filter paper. The yield amounts to 6·5—7·4 grams, corresponding with 87—99 per cent. of the theoretical. For analysis it must not be mixed, but only carefully covered with cupric oxide:

0·1121 gave 30·9 c.c. N_2 at 15° and 756·1 mm. N = 32·39.

$C_4H_6O_4N_4$ requires N = 32·19 per cent.

Oxalylbismethylnitrosoamide melts at about 66°,* with evolution of gas; the point of decomposition greatly depends on the rate of heating. On spontaneous evaporation the ethereal solution deposits beautiful, yellowish-red crystals, which on pulverising become pale yellow. The nitrosoamide shows Liebermann's nitroso-reaction. It is almost insoluble in cold water, somewhat soluble in light petroleum, readily so in methyl and ethyl alcohols, very readily soluble in ether, and exceedingly so in benzene, chloroform, acetone, or acetic acid. It possesses only a very faint odour, but nevertheless its vapour and dust irritate the mucous membranes of the nose and the eyes. On dissolving the crystals in ether or acetic acid at the ordinary temperature, a crackling noise is heard.

The nitrosoamide is very unstable. The clear crystals become somewhat opaque, even in the course of a day; on keeping longer they lose their sharp edges, and finally fall into a yellow powder. When kept for some time in a closed bottle they develop a strong odour of the decomposition products.

Crystals which have been prepared some time previously show a remarkable phenomenon; when placed on a piece of paper on the hand, they make occasional jumping movements, probably the result of decomposition.

Decomposition by Alkali Hydroxides.—Methyl-alcoholic potassium hydroxide, when added in excess to an ethereal solution of the nitrosoamide, produces a violent evolution of gas:

$$[\cdot CO\cdot N(NO)\cdot CH_3]_2 + 2KOH \longrightarrow (CO_2K)_2 + 2CH_2N_2.$$

When the reaction is carried out in a distilling flask with dropping funnel and condenser, the yellow ethereal solution of diazomethane † distils over.

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* The melting points of the new compounds were all taken with short Anschütz thermometers.

† In this and subsequent experiments, diazomethane was recognised by its behaviour towards water and inorganic acids. Unless the solution contained ammonia, the reaction with ethereal iodine was also carried out, which produced a viscous liquid possessing the odour of methylene iodide.

The white substance remaining in the flask was identified as potassium oxalate.

Decomposition by Ammonia.—Hitherto it does not seem to have been noticed that methylnitrosoamides when treated with ammonia yield diazomethane; yet the reaction takes place readily:

$$[\cdot CO\cdot N(NO)\cdot CH_3]_2 + 2NH_3 \longrightarrow (\cdot CO\cdot NH_2)_2 + 2CH_2N_2.$$

A current of dry ammonia was passed through the ethereal solution of the nitrosoamide. Heat was developed, and diazomethane distilled over. In the distilling flask a white substance separated, which after crystallising from boiling water was identified as oxamide. From 0·8 gram of the nitroso-compound 0·4 gram was obtained, corresponding with the theoretical yield.

The nitrosoamide, when moistened with alcohol, is also readily decomposed by aqueous ammonia. The amount of diazomethane obtained by this reaction is, however, small, owing to the decomposing action of the water.

Decomposition by Substituted Ammonia.—*Aniline* reacts in the same way as ammonia, but much less violently:

$$[\cdot CO\cdot N(NO)\cdot CH_3]_2 + 2PhNH_2 \longrightarrow (CO\cdot NHPh)_2 + 2CH_2N_2.$$

The nitrosoamide readily dissolves in aniline, with marked development of heat. For moderating the reaction both substances were mixed in ethereal solution, when diazomethane distilled over, and a white product crystallised. The latter was identified as oxanilide by its melting point (245°, uncorr.), which was not changed by mixing with a known specimen.

Hydrazine reacts violently with the nitrosoamide:

$$[\cdot CO\cdot N(NO)\cdot CH_3]_2 + 2NH_2\cdot NH_2 \longrightarrow (\cdot CO\cdot NH\cdot NH_2)_2 + 2CH_2N_2.$$

When adding the theoretical amount of hydrazine hydrate to the ethereal solution of the nitrosoamide, diazomethane escaped immediately, and oxalyldihydrazide (decomposing at 233°, uncorr.) separated. 0·2 Gram of the nitroso-compound yielded 0·12 gram of hydrazide, or 88 per cent. of the theoretical amount.

The reaction with *phenylhydrazine* is analogous:

$$[\cdot CO\cdot N(NO)\cdot CH_3]_2 + 2PhNH\cdot NH_2 \longrightarrow (\cdot CO\cdot NH\cdot NHPh)_2 + 2CH_2N_2.$$

On mixing both substances in ethereal solution, diazomethane distilled over, and oxalylbisphenylhydrazide (m. p. 273—274°, uncorr.) crystallised. Yield, 0·23 gram from 0·2 gram of nitroso-compound, or 74 per cent. of the theoretical.

Electro-reduction.—The cathodic liquid is 60 c.c. of 50 per cent. acetic acid, to which 3 grams of the nitrosoamide dissolved in 15 c.c. of acetic acid are gradually added during the reduction. The cathode is a cylinder of tinned copper-wire gauze (circumference 16 cm., height 8 cm.), and the anode a spiral of lead tubing,* through which a current of cold water is passed. The anodic liquid, consisting of 5 per cent. sulphuric acid, is separated from the cathodic liquid in the usual way by a porous cell. The apparatus is placed in ice, in order that the temperature of the cathodic liquid may not exceed 20° during the reduction. The strength of the current is kept at about 2—3 amperes. It is advisable to use an excess of current, for example, 80 ampere-minutes, instead of 74 ampere-minutes, for each gram of nitroso-compound, because a little hydrogen always escapes during the reduction.

Finally, the colourless solution shows the ordinary reactions of secondary *as*-hydrazines towards Fehling's liquid, silver nitrate, or mercuric oxide. In order to separate the hydrazide, the solution is partly neutralised with sodium carbonate, and shaken with an alcoholic solution of benzaldehyde, when the hydrazone separates after some time.

From 2·8 grams of the nitrosoamide there was obtained only 0·2 gram of hydrazone, corresponding with 4 per cent. of the theoretical yield. After crystallisation from alcohol the product was analysed:

0·1578 gave 0·3885 CO_2 and 0·0789 H_2O. $C=67·14$; $H=5·60$.
0·126 „ 19·45 c.c. N_2 (moist) at 16·8° and 747 mm. $N=17·54$.
$C_{18}H_{18}O_2N_4$ requires $C=67·04$; $H=5·63$; $N=17·39$ per cent.

Oxalylbisbenzylidenemethylhydrazone, $(\cdot CO\cdot NMe\cdot N\colon CHPh)_2$, when crystallised from aqueous alcohol, forms small, delicate plates, melting sharply at 210°. It is very sparingly soluble in water, light petroleum, or ether, readily so in methyl and ethyl alcohols, and very readily so in benzene, acetic acid, acetone, or chloroform.

Because various attempts to prepare this hydrazone in a different way (from oxalyldihydrazide, oxalylbisbenzylidenehydrazone, or benzylidenemethylhydrazone) were unsuccessful, another proof of its constitution was given by hydrolysis. Boiling hydrochloric acid liberated slowly benzaldehyde, which was identified as benzylideneazine (m. p. 93°), whilst the remaining solution gave the reactions of oxalic acid and methylhydrazine:

$$(\cdot CO\cdot NMe\cdot N\colon CHPh)_2 + 4H_2O = (\cdot CO_2H)_2 + 2MeNH\cdot NH_2 + 2Ph\cdot CHO.$$

II.—*Succinylbismethylnitrosoamide*, $NO\cdot NMe\cdot CO\cdot CH_2\cdot CH_2\cdot CO\cdot NMe\cdot NO$.

The required succinylbismethylamide was prepared from methylamine and dimethyl succinate, which reacts much more readily than diethyl succinate.

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* Failing pure lead, tubing of lead-tin composition may take its place.

Dimethyl succinate (22 grams), when gradually added to aqueous methylamine (28·3 grams of a 33 per cent. solution), produces a development of heat, and after shaking for a few minutes the layer of ester is dissolved. The liquid is heated for three hours in a closed vessel at about 70° in order to complete the reaction, and finally evaporated on a water-bath. The residue, when crystallised from a mixture of ether and methyl alcohol, gives 14·5 grams of succinylbismethylamide (m. p. 175°), or 67 per cent. of the theoretical yield. Heating of the mixture in a closed vessel may also be omitted without considerable influence on the yield (13·4 grams were obtained, or 62 per cent.).

The amide is nitrosated by dissolving 4 grams in 15 c.c. of cold glacial acetic acid, and passing through this solution, while cooling with water, a current of nitrous anhydride. During the reaction a part of the nitrosoamide crystallises. In contradistinction from the corresponding oxalic derivatives, the methylnitrosoamide of succinic acid is thus less soluble than the methylamide itself. As soon as a notable quantity of the nitrosoamide has separated and the solution has a dark green colour, the reaction is stopped, because the nitrous anhydride, when reacting too long, possibly might attack the hydrogen atoms attached to carbon.

The nitrosoamide, which separates completely on adding ice and water, is collected, washed with water, and dried. Although not necessary, the product may be purified by precipitating either the cold acetic solution with water or the acetone solution with light petroleum. It may also be crystallised from boiling ether:

0·1262 gave 30·3 c.c. N_2 (moist) at 18° and 764·5 mm. N = 27·78.
$C_6H_{10}O_4N_4$ requires N = 27·73 per cent.

Succinylbismethylnitrosoamide usually crystallises in small, delicate, pale yellow plates with a pink lustre, melting with evolution of gas at 110° (somewhat depending on the rate of heating), and showing Liebermann's test. From its ethereal solution, when evaporated spontaneously, it separates in large, flat, pinkish-yellow crystals.

The compound is more stable than the corresponding oxalyl derivative, and less irritating to the mucous membranes. In the dark it may be kept for several days; on exposure to light it is soon coloured green at the surface.

The solubility is in most cases less than that of the oxalyl compound. It dissolves very sparingly in cold water, somewhat more in light petroleum, sparingly in methyl and ethyl alcohols or ether, and readily in benzene, acetone, acetic acid, or chloroform.

Decomposition by Alkali Hydroxides.—The nitrosoamide, when treated in methyl-alcoholic solution with a small excess of potassium hydroxide, evolves diazomethane:

$$[\cdot CH_2\cdot CO\cdot N(NO)\cdot CH_3]_2 + 2KOH \longrightarrow (\cdot CH_2\cdot CO_2K)_2 + 2CH_2N_2.$$

In order to complete the reaction, the mixture was heated slightly. The alcoholic liquid was acidified with hydrochloric acid, and on evaporation to dryness left a mixture of potassium chloride and succinic acid. The latter substance, obtained by extraction with boiling ether, had the same melting point (185°, not changed by mixing) and boiling point (230°, uncorr.) as a specimen of pure succinic acid.

Decomposition by Ammonia.—Ammonia acts in the same way as with the oxalyl compound, but less readily:

$$[\cdot CH_2\cdot CO\cdot N(NO)\cdot CH_3]_2 + 2NH_3 \longrightarrow (\cdot CH_2\cdot CO\cdot NH_2)_2 + 2CH_2N_2.$$

The nitrosoamide was suspended in methyl alcohol and ether, and treated with a current of dry ammonia. With evolution of diazomethane, the liquid deposited a white substance, which was identified as succinamide.

Decomposition by Substituted Ammonia.—The nitroso-compound, when suspended in methyl alcohol and treated with the theoretical amount of *hydrazine hydrate*, gave off diazomethane, with formation of succinyldihydrazide, which on addition of ether was completely separated in small plates (m. p. 165°). From 0·5 gram of the nitrosoamide 0·27 gram of hydrazide was obtained, or 75 per cent. of the theoretical amount.

The reaction with *phenylhydrazine* was carried out in the same way, but required slightly heating. Diazomethane and succinylbisphenylhydrazide (m. p. 200°, decomp.) were produced.

Electro-reduction.—The cathodic liquid is 30 c.c. of 50 per cent. acetic acid, to which 2·5 grams of the nitrosoamide dissolved in 40—50 c.c. of acetic acid are gradually added. The other conditions are as described above for the oxalyl compound. Instead of the theoretical amount of 65 ampere-minutes there are passed through the solution 70 ampere-minutes for each gram of nitrosoamide.

The liquid obtained shows the hydrazine reactions, and when shaken with an alcoholic benzaldehyde solution deposits after some time the hydrazone. Yield, 0·5 gram, or 12 per cent. of the theoretical:

0·1675 gave 22·85 c.c. N_2 at 11° and 754·5 mm. N = 16·07.

$C_{20}H_{22}O_2N_4$ requires N = 16·00 per cent.

Succinylbismethylbenzylidenehydrazone,

$(\cdot CH_2\cdot CO\cdot NMe\cdot N{:}CHPh)_2$,

crystallises from methyl alcohol in small, white needles, melting sharply at 193·5°. They dissolve very sparingly in water, light petroleum, or ether, fairly readily in methyl and ethyl alcohols, readily in acetone, benzene, or acetic acid, and extremely easily in chloroform. Hydrolysis by boiling hydrochloric acid yielded succinic acid (m. p. 185°), methylhydrazine, and benzaldehyde (benzylideneazine, m. p. 93°).

In conclusion, the author desires to express his hearty thanks to the Committee of the Davy-Faraday Research Laboratory of the Royal Institution for the facilities afforded him in working there.

DAVY-FARADAY RESEARCH LABORATORY.

LXIX.—*The Reciprocal Influence of Unsaturated Centres and its Effect on the General Absorptive Power of Compounds.*

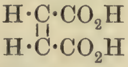
By ALEXANDER KILLEN MACBETH, ALFRED WALTER STEWART, and ROBERT WRIGHT.

WHEN one examines the influences which appear to produce most effect on the general absorptive power of simple organic compounds, three factors seem to stand out above others. In the first place, an increase in the number of methylene groups in a compound tends to raise its power of general absorption, as was shown by Hartley; secondly, the production of an unsaturated centre, or in other words the presence of residual affinity in the molecule, greatly increases the general absorptive power. This was shown by Hartley in his earlier researches. Thirdly, the conjugation of two unsaturated centres in the manner postulated by Thiele in his partial valency theory produces a large increase in general absorption, as was proved by the previous work of the present authors and their collaborators.

Following this last line, it appeared of interest to determine whether two unsaturated centres in the same molecule, although not conjugated in the Thiele sense, could vary in their influence on the absorptive power of the compound containing them if their relative positions were altered; and in the present paper some data are given which throw some light on the point.

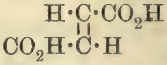
In the first place, since a change of structure might in itself be sufficient to alter general absorptive power, it is necessary to examine one or two cases of stereoisomerides in which this factor is excluded. In these examples we can trace the effect produced by the change in the relative positions of two unsaturated groups without introducing the influence of constitutional change and the consequent rearrangement of affinity between the different atoms of the molecule.

The spectra of maleic and fumaric acids have been described by Magini (*J. Chim. phys.*, 1904, **2**, 410); those of citraconic and mesaconic acids as well as the other two have been examined by Stewart (Trans., 1907, **91**, 199), and in both pairs it was found that the fumaroid form had a greater absorptive power than the maleinoid type. An examination of the space formulæ will show that in each case there is a double bond in the centre of the model which is conjugated in the Thiele sense with the carbonyl groups of each carboxyl radicle. The effect of this double bond may be reasonably supposed to be similar in each pair, so that for the sake of comparison its influence may be neglected. This leaves us to consider the effects of the unsaturated carboxyl radicles:



$$\begin{array}{l} H\cdot C\cdot CO_2H \\ \quad \| \\ H\cdot C\cdot CO_2H \end{array}$$

Maleic acid.



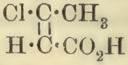
$$\begin{array}{r} H\cdot C\cdot CO_2H \\ \| \quad\quad\;\; \\ CO_2H\cdot C\cdot H \end{array}$$

Fumaric acid.

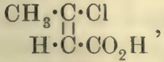
In changing from the maleinoid form to the fumaroid form, the relative positions of two important centres of residual affinity (the carboxyl groups) have been shifted, and this, as we have seen, is accompanied by a change in the absorptive power of the substance. Similarly, when active tartaric acid is converted into the meso-form the relative positions of the carboxyl groups are rearranged, and in this case also a large difference between the absorptive power of the two compounds is found (Magini, *loc. cit.*; Stewart, Trans., 1907, **91**, 1539).

The question now arises: If we cause an analogous isomeric change to take place in a molecule which contains only *one* unsaturated centre (such as the carboxyl radicle), shall we find that the mere isomerisation is sufficient to produce this change in absorptive power, or will the absence of a reciprocal action of *two* unsaturated centres be parallelled by the absence of a great change in absorptive power?

To test this we examined the spectra of the two isomeric β-chlorocrotonic acids:

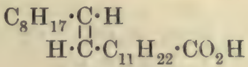


$$\begin{array}{l} Cl\cdot C\cdot CH_3 \\ \quad \| \\ H\cdot C\cdot CO_2H \end{array}$$



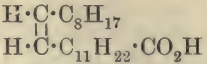
$$\begin{array}{l} CH_3\cdot C\cdot Cl \\ \qquad \| \\ \;\; H\cdot C\cdot CO_2H \end{array},$$

and we find that they are very similar and differ from each other much less than do maleic and fumaric or citraconic and mesaconic acids. The spectra of erucic and brassidic acids were also examined, and in this case also the differences were very slight:



$$\begin{array}{l} C_8H_{17}\cdot C\cdot H \\ \qquad\quad \| \\ \quad H\cdot C\cdot C_{11}H_{22}\cdot CO_2H \end{array}$$

Erucic acid.

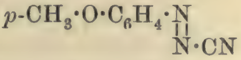


$$\begin{array}{l} H\cdot C\cdot C_8H_{17} \\ \quad\ \| \\ H\cdot C\cdot C_{11}H_{22}\cdot CO_2H \end{array}$$

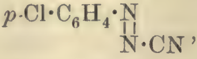
Brassidic acid.

Let us imagine the carboxyl at one end of the chain as fixed. Then in the case of maleic and fumaric acids, as well as in that of citraconic and mesaconic acids, in the change from the maleinoid to the fumaroid form the position of a second carboxyl radicle with respect to the first is shifted, and the relative positions of two large unsaturated centres are thus altered. On the other hand, in the case of the chlorocrotonic acids the relative positions of the carboxyl group and a fairly saturated centre like the chlorine atom or the methyl radicle only are changed; and in the case of erucic and brassidic acids merely the position of a saturated group with respect to the carboxyl is changed. It thus appears clear that in order to obtain a marked difference between two stereoisomerides these substances must contain *two* unsaturated centres, the relative positions of which in space are different in the two isomeric forms.

Similar results are found when the curves given by Dobbie and Tinkler (Trans., 1905, **87**, 273) for the isomeric compounds of the diazo-series are examined. These authors found that the *syn*- and *anti*-modifications of potassium benzenediazosulphonate had identical spectra. An examination of the formula $C_6H_5\cdot N\colon N\cdot SO_3K$ shows that here we have to do with only one group which can reasonably be called unsaturated; for the sulphonic radicle, $\cdot SO_3K$, on account of its reactions, can hardly be classed as very unsaturated. Hence in this case we have a shift of a *saturated* centre with regard to an unsaturated one (the phenyl radicle), and consequently no great change in spectra could be expected in passing from one compound to the other. On the other hand, when we take the case of such compounds as:



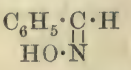
$$\begin{array}{l} p\text{-}CH_3\cdot O\cdot C_6H_4\cdot N \\ \qquad\qquad\qquad\quad\ \| \\ \qquad\qquad\qquad\quad N\cdot CN \end{array}$$



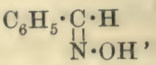
$$\begin{array}{l} p\text{-}Cl\cdot C_6H_4\cdot N \\ \qquad\qquad\ \ \| \\ \qquad\qquad\ N\cdot CN, \end{array}$$

we see that the change from the *syn*- to the *anti*-form in either case would entail the change in position of the unsaturated cyano-group with regard to the unsaturated phenyl nucleus, and hence we should expect to find a difference between the general absorptive powers of the two forms. This difference is observed in practice, so that in this case also the rule appears to hold good.

A final example may be quoted. If we examine the formulæ of the two benzaldoximes:



$$\begin{array}{l}C_6H_5\cdot C\cdot H\\ \qquad\;\;\|\\ \;\;HO\cdot N\end{array}$$



$$\begin{array}{l}C_6H_5\cdot C\cdot H\\ \qquad\;\;\|\\ \qquad\;\;N\cdot OH\end{array},$$

we see that in passing from the one form to the other the relative positions of the phenyl and hydroxyl radicles are altered. Now, although the phenyl radicle is unsaturated, the hydroxyl group can hardly be called a centre of much residual affinity; and hence we should expect to find very little difference between the absorptive powers of the two isomerides. Hartley and Dobbie (Trans., 1900, **77**, 509) found that the two substances gave identical spectra; so that in this case also our views appear to hold good.

Hantzsch (*Ber.*, 1910, **43**, 1656) has examined several cases of stereoisomeric oximes, and finds that the spectra of the isomeric forms of chlorotoluquinoneoxime are identical, as are those of *p*-nitrobenz*syn*aldoxime and the *anti*-isomeride. The case of the two stereoisomeric oximes of benzil described by him hardly comes within the scope of our present work, as there are four centres of residual affinity within the molecule, and consequently it is hardly possible to sift out the exact influence which should be ascribed to each factor. It should be pointed out that in reference to the special case of homochromoisomerism, Hantzsch draws conclusions similar to those put forward above.

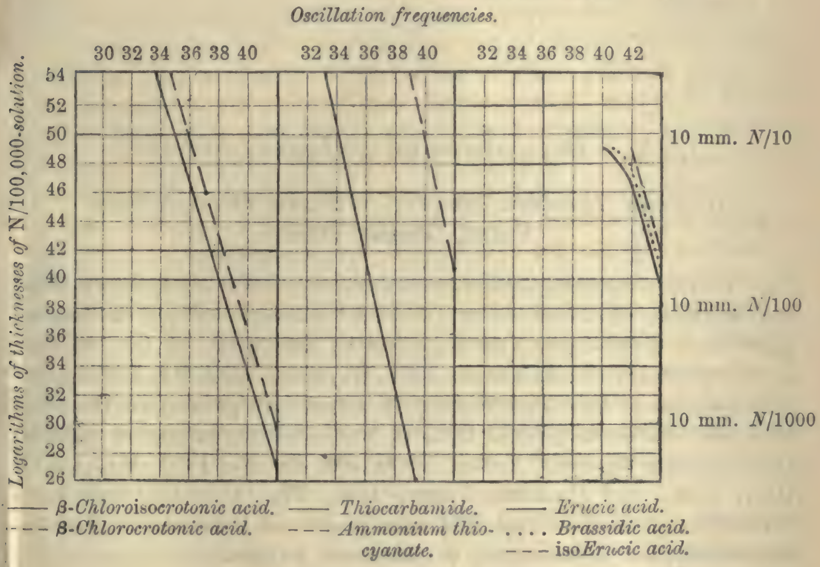
So far we have investigated cases in which the alteration in residual affinity is caused by the relative shifting of two unsaturated centres; but there is another line in which the problem may be attacked, namely, by the comparison of two isomerides, one of which contains fewer centres of residual affinity than the other. If we examine the formulæ of thiocarbamide and ammonium thiocyanate, we find that the former has at least two unsaturated centres in its molecule, namely, the two amino-groups, whilst in ammonium thiocyanate the ·CNS-group is the only centre of residual affinity, since the ammonium radicle is obviously fully saturated:

$NH_2\cdot CS\cdot NH_2$	$NH_4\cdot CNS$
Thiocarbamide.	Ammonium thiocyanate.

Hence we should expect to find that there is a very marked difference between their absorption spectra; and as can be seen from the curves this is actually the case.

We have thus shown that in order to produce any marked difference between the general absorption spectra of isomeric compounds it is necessary that the relative positions of two unsaturated centres within the molecule should be changed. From this we are led to inquire what influence is exerted by molecular symmetry on general absorptive power; also, since it seems advisable to eliminate disturbing influences so far as possible, we propose to examine a series of isomeric open-chain acids and esters with a view to discover whether flaccid chains of this type obey the same rule as the more rigidly braced ones containing the double bond.

Before concluding, we may mention two points which arose incidentally in the course of this work. In addition to the two substances, erucic and brassidic acids, we prepared the third isomeride, *iso*-erucic acid. As can be seen from the figure, its absorptive power is less than that of either erucic or brassidic acid.



We have also prepared the two forms of thiocarbamide, and examined their spectra. These prove to be identical, so that it seems probable that the difference between the two forms is merely a crystallographic one.

Conclusions.

(1) If a molecule contains an unsaturated centre U (such as the carboxyl group) and a saturated radicle S, it is found that when S is shifted in space with respect to U no great change takes place in the general absorptive power of the molecule.

(2) If the molecule contains two unsaturated centres, U and U_1, a change in their relative positions produces marked effects on the molecule's power of general absorption. It is therefore probable

that in order to alter a molecule's power of general absorption the relative positions of two unsaturated centres within it must be altered.

(3) In the case of the structural isomerides thiocarbamide and ammonium thiocyanate, the molecule containing two unsaturated centres (thiocarbamide) has a greater power of general absorption than that which contains only one unsaturated centre.

We desire to express our thanks to Mr. C. R. Crymble, B.A., B.Sc., for assistance during the course of the work.

THE SIR DONALD CURRIE LABORATORIES,
THE QUEEN'S UNIVERSITY OF BELFAST.

LXX.—*Derivatives of* p-*Hydroxystilbene.*

By JOHN THEODORE HEWITT, WILLIAM LEWCOCK, and FRANK GEORGE POPE.

As a result of spectrographic measurements, it has been shown that the addition of alkali to an alcoholic solution of an azophenol produces a displacement of the selective absorption to the red end of the spectrum (Tuck, Trans., 1907, **91**, 449; 1909, **95**, 1809); the displacement of the absorption is, however, far greater in the case of *p*-nitrobenzeneazophenol than in that of benzeneazophenol itself (Hewitt and Mitchell, Trans., 1906, **89**, 13, 17; 1907, **91**, 1251; Baly, Tuck, and Marsden, Trans., 1910, **97**, 1494). Hewitt and Mitchell suggest that the difference is due to the salts of *p*-nitrobenzeneazophenol possessing a quinonoid structure:

$$KO\cdot NO{:}C_6H_4{:}N\cdot N{:}C_6H_4{:}O;$$

from this view Baly, Tuck, and Marsden dissent.

It has been shown (F. G. Pope, Trans., 1908, **93**, 532) that whilst the condensation product of benzaldehyde and *p*-aminophenol gives faintly yellow alkaline solutions, the corresponding alkaline solutions of *p*-nitrobenzylidene-*p*-aminophenol are deep orange-red; in this case the formation of a quinonoid salt has been suggested. Evidently the replacement of one nitrogen atom in the azophenols by a methine group involves a higher oscillation frequency of the molecule; but the same sort of shift is produced on adding alkali to benzylidene-*p*-aminophenol as that which occurs with benzeneazophenol, and in both cases the presence of a *p*-nitro-group conditions a greater displacement of the absorption when alkali is added. In these circumstances it appeared desirable to examine the corresponding stilbene compounds so as to complete the series:

$C_6H_5\cdot N{:}N\cdot C_6H_4\cdot OH$; $NO_2\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot OH$;
$C_6H_5\cdot CH{:}N\cdot C_6H_4\cdot OH$; $NO_2\cdot C_6H_4\cdot CH{:}N\cdot C_6H_4\cdot OH$;
$C_6H_5\cdot CH{:}CH\cdot C_6H_4\cdot OH$; $NO_2\cdot C_6H_4\cdot CH{:}CH\cdot C_6H_4\cdot OH$.

EXPERIMENTAL.

In preparing the materials necessary for this work, syntheses from phenylacetic acid and its *p*-nitro-derivative with suitable aldehydes were employed. Walther and Wetzlich (*J. pr. Chem.*, 1900, [ii], **61**, 181) obtained *α-p*-nitrophenylcinnamic acid by heating *p*-nitrophenylacetic acid and benzaldehyde to 205°, but were unable to effect a smooth removal of carbon dioxide; many syntheses of phenanthrene derivatives in which stilbene compounds are intermediately formed have been carried out by R. Pschorr (*Ber.*, 1900, **33**, 176, etc.), who follows Perkin's synthesis of cinnamic acid in that he heats the sodium salt of the substituted phenylacetic acid with the necessary aldehyde and acetic anhydride. During the progress of the present work a paper appeared by Pfeiffer and Sergiewskaja (*Ber.*, 1911, **44**, 1107), in which the condensation of aldehydes and substituted phenylacetic acids was effected by piperidine, and of this reaction we have made considerable use. It is noteworthy that whilst Walther and Wetzlich employed a temperature of 205° to effect the condensation of *p*-nitrophenylacetic acid and benzaldehyde, addition of piperidine causes reaction to take place at 150—160°, and, moreover, effects the removal of carbon dioxide, so that Pfeiffer and Sergiewskaja isolated quite fair yields of nitrostilbene.

p-*Hydroxystilbene*, $C_6H_5\cdot CH{:}CH\cdot C_6H_4\cdot OH$.—Five grams of *p*-hydroxybenzaldehyde, 5 grams of phenylacetic acid, and 1 c.c. of piperidine were heated for five hours to 150°. From the resulting product, unchanged phenylacetic acid was extracted by hot dilute sodium carbonate solution, and the residue was dissolved in hot dilute aqueous sodium hydroxide; on cooling, the colourless, crystalline sodium salt of hydroxystilbene was deposited. This salt separates readily from its solutions on addition of sodium hydroxide; the free hydroxystilbene was liberated by dilute hydrochloric acid, and crystallised from dilute alcohol:

0·1193 gave 0·3746 CO_2 and 0·0656 H_2O. C=85·6; H=6·1.

$C_{14}H_{12}O$ requires C=85·7; H=6·1 per cent.

This substance is a colourless, crystalline powder, which melts at 184·5° (uncorr.), and is readily soluble in alcohol; the solution in concentrated sulphuric acid is red.

p-*Methoxystilbene*, $C_6H_5\cdot CH\dot{:}CH\cdot C_6H_4\cdot O\cdot CH_3$.—Oglialoro obtained this compound from the corresponding carboxylic acid by distillation (*Jahresber.*, 1879, 731); Funk and von Kostanecki eliminated carbon dioxide by allowing the acid to remain for some days with hydriodic acid (D 1·96) in the cold (*Ber.*, 1905, **38**, 940). It has now been found that piperidine may be used for effecting removal of carbon dioxide from the carboxylic acid; heating in this case is more prolonged than if the piperidine is simply to be used for condensation of anisaldehyde and phenylacetic acid. When piperidine is employed, purification of the product can be effected by dissolving the crude product in hot light petroleum; on cooling, tarry matter is first deposited, and is fractionally removed. Repeating this process several times and finally crystallising from alcohol gives a product melting at 136°, as observed by Oglialoro; the compound is very soluble in hot alcohol, but separates nearly completely on cooling.

Methoxystilbene can also be prepared from hydroxystilbene by dissolving it in dilute alkali and warming gently with methyl sulphate. Probably Oglialoro's method is the most convenient; it is simple, and gives reasonable yields.

Methoxystilbene resembles hydroxystilbene in giving a red coloration with concentrated sulphuric acid; possibly quinonoid oxonium salts:

$$C_6H_5\cdot CH_2\cdot CH\dot{:}C_6H_4\dot{:}O(H \text{ or } CH_3)\cdot SO_4H,$$

corresponding with the salts of the azophenols with mineral acids, are produced.

α-Phenyl-p-*methoxycinnamic Acid*,

$$C_6H_5\cdot C(CO_2H)\dot{:}CH\cdot C_6H_4\cdot O\cdot CH_3.$$

—Oglialoro condensed anisaldehyde and phenylacetic acid, using Perkin's method; piperidine can, however, be conveniently employed. One c.c. of piperidine is added to 10 grams of an equimolecular mixture of anisaldehyde and phenylacetic acid; after heating for three hours at 150°, the mass solidifies on cooling. Washing with cold glacial acetic acid removes tarry impurities; a solution of the residue in hot alcohol deposits *α*-phenyl-*p*-methoxycinnamic acid in colourless needles on cooling. (Found, C = 75·1; H = 5·6. Calc., C = 75·4; H = 5·5 per cent.)

p-*Nitrostilbene*.—The requisite material was prepared by the method of Pfeiffer and Sergiewskaja (*loc. cit.*, 1109); the specimen used melted, in agreement with their determination, at 155°.

p-*Nitro*-p′-*hydroxystilbene*, $NO_2\cdot C_6H_4\cdot CH\dot{:}CH\cdot C_6H_4\cdot OH$.—This compound was obtained by boiling *α*-*p*-nitrophenyl-*p*-acetoxycinnamic acid with equal volumes of alcohol and fuming hydrochloric acid for four hours under reflux; not only was the acetyl group hydrolysed, but carbon dioxide was also eliminated from the carboxyl group. The alcoholic solution was poured into water, and the resulting precipitate crystallised from dilute alcohol, when it formed yellow needles melting at 193° (uncorr.):

0·1146 gave 0·2943 CO_2 and 0·0439 H_2O. C = 70·0; H = 4·2.
0·1414 „ 7·4 c.c. N_2 at 17·5° and 760 mm. N = 6·0.
$C_{14}H_{11}O_3N$ requires C = 69·7; H = 4·6; N = 5·8 per cent.

A good yield of the compound may also be obtained by Pfeiffer's method; the reaction product is dissolved in hot glacial acetic acid, from which solution cold water precipitates the nitrohydroxystilbene. The substance is subsequently crystallised from dilute alcohol or xylene.

Nitrohydroxystilbene dissolves in alcohol with a pale yellow colour; addition of alkali to the solution makes it assume a deep brown shade. Attempts to methylate an alkaline solution by methyl sulphate were unsuccessful, although the conditions were similar to those obtaining when hydroxystilbene was successfully methylated.

α-p-*Nitrophenyl*-p-*acetoxycinnamic Acid*,

$$NO_2\cdot C_6H_4\cdot C(CO_2H)\colon CH\cdot C_6H_4\cdot O\cdot CO\cdot CH_3.$$

—Eighteen grams of *p*-nitrophenylacetic acid were dissolved in 100 c.c. of *N*-sodium hydroxide, the solution evaporated to dryness, and the residual salt boiled for eight hours with 12 grams of *p*-hydroxybenzaldehyde and 50 grams of acetic anhydride (temperature of oil-bath 170°). The mass was extracted by boiling with dilute alcohol (three hours), the solution poured into water, and the precipitate allowed to settle; this takes some time. From the precipitate the acid was extracted with sodium carbonate solution, reprecipitated with hydrochloric acid, and crystallised from a mixture of carbon tetrachloride and glacial acetic acid. It forms a pale yellow, crystalline powder, melting at 205° (uncorr.):

0·0883 gave 0·2009 CO_2 and 0·0285 H_2O. C = 62·1; H = 3·7.
$C_{17}H_{13}O_6N$ requires C = 62·4; H = 3·9 per cent.

p-*Nitro*-p′-*methoxystilbene*, $NO_2\cdot C_6H_4\cdot CH\colon CH\cdot C_6H_4\cdot O\cdot CH_3$.—Elimination of carbon dioxide by heating the corresponding carboxylic acid with 66 per cent. sulphuric acid gives a poor yield, much of the substance being charred; similar results were obtained on boiling with concentrated hydrochloric acid. A small yield is also obtained when the acid is heated above its melting point; the reaction gives a somewhat better result when the acid is distilled under diminished pressure. It may be noticed that Walther and Wetzlich (*loc. cit.*) were unable to obtain nitrostilbene from the corresponding carboxylic acid.

Pfeiffer's method gives a good yield of pure material. Eight grams of nitrophenylacetic acid, 6 grams of anisaldehyde, and 2 c.c. of piperidine were heated for four hours at 150—170°; any unaltered material was extracted with hot dilute sodium hydroxide, the residue dissolved in hot glacial acetic acid, and on cooling the desired substance was obtained in a crystallised condition. After recrystallisation from glacial acetic acid, nitromethoxystilbene formed beautiful, orange needles, melting at 162° (uncorr.):

0·1035 gave 0·2686 CO_2 and 0·0455 H_2O. C=70·8; H=4·8.

$C_{15}H_{13}O_3N$ requires C=70·6; H=5·0 per cent.

The substance dissolves fairly readily in benzene, sparingly in alcohol; it is reddened by concentrated sulphuric acid. Attempts at isolating oxonium salts were unsuccessful.

*a-*p*-Nitrophenyl-*p*-methoxycinnamic Acid,*

$NO_2\cdot C_6H_4\cdot C(CO_2H)\colon CH\cdot C_6H_4\cdot O\cdot CH_3$.

—Eighteen grams of nitrophenylacetic acid were converted into the sodium salt, and heated for eight hours with 13·5 grams of anisaldehyde and 50 grams of acetic anhydride. The excess of acetic anhydride was destroyed by dilute alcohol; the product obtained by pouring into water was tarry at first, but solidified on keeping. The acid was purified by solution in sodium carbonate, reprecipitation by hydrochloric acid, and crystallisation from alcohol; it forms an orange, crystalline powder, melting at 231° (uncorr.):

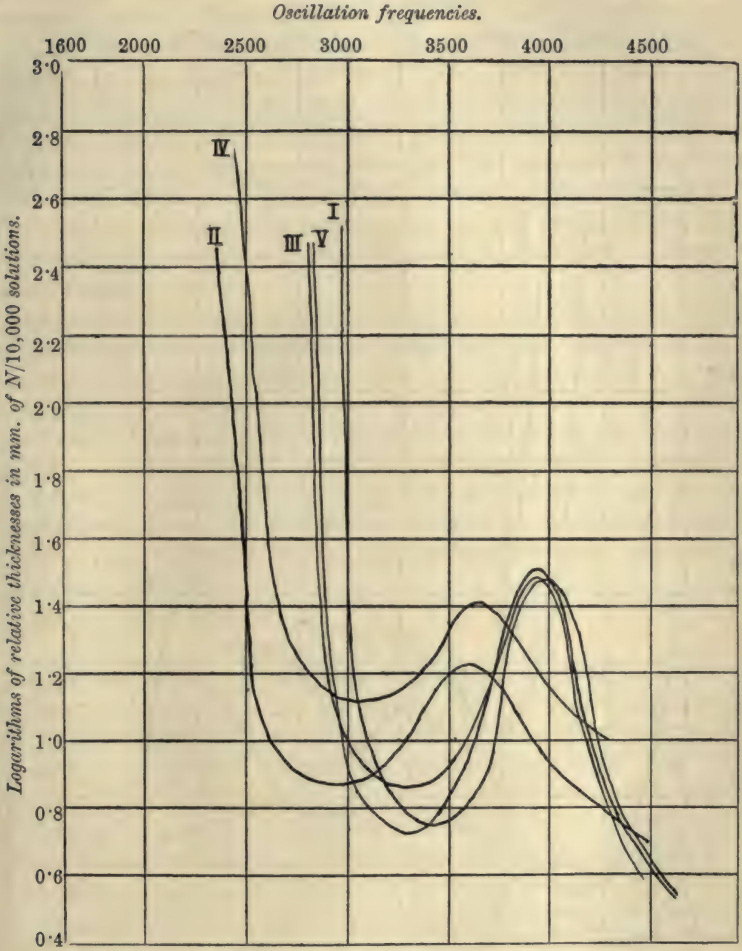
0·1188 gave 0·2849 CO_2 and 0·0493 H_2O. C=64·5; H=4·6.

$C_{16}H_{13}O_5N$ requires C=64·2; H=4·3 per cent.

Absorption Spectra.

On reference to the two figures it will be seen that there is in each case a well marked absorption band. Taking the heads of the absorption bands, it is noticeable that the introduction of the hydroxyl group into stilbene lowers the oscillation frequency by about 70 units, the nitro-group by about 500 units. Fig. 1 shows that the oscillation frequencies of hydroxy- and methoxy-stilbene are fairly close together, but on converting the former into the sodium salt the oscillation frequency is reduced between 200 and 300 units. In Fig. 2 stilbene is compared with nitrostilbene and derivatives of the latter substance. Again it will be noticed that the heads of the absorption bands of the hydroxy- and methoxy-derivatives lie not very far from that of the parent nitrostilbene, but that where the hydroxy-compound is converted into the sodium salt a shift of between 500 and 600 units occurs. The differences in oscillation frequency are even more marked when considered in the following manner: The effect of introducing a nitro-group into stilbene is to shift the head of the band by about 500 units; comparing hydroxystilbene and its nitro-derivative, the shift is between 600 and 700 units; but between the heads of the bands in the cases of the sodium salts of hydroxystilbene and its nitro-derivative there is a difference of between 900 and 1000 units. The changes are similar to those observed in the azo-series, and it may be that the difference in behaviour is accounted for by the sodium salts of

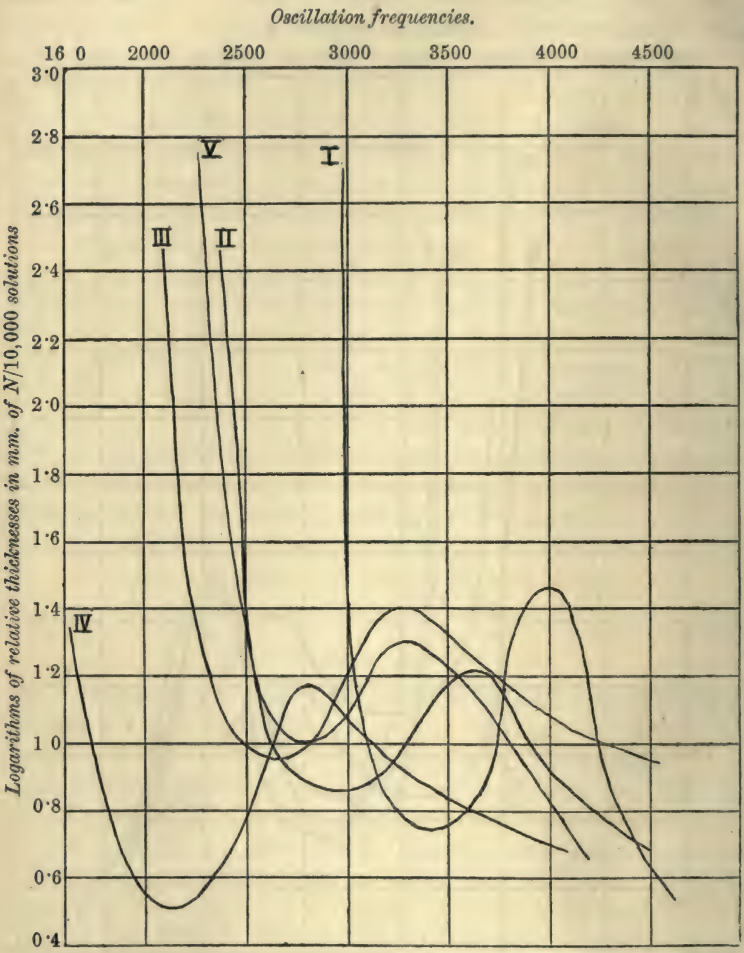
FIG. 1.



I. *Stilbene in alcoholic solution.*
II. *Nitrostilbene in alcoholic solution.*
III. *Hydroxystilbene in alcoholic solution.*
IV. ,, ,, *sodium hydroxide.*
V. *Methoxystilbene in alcoholic solution.*

hydroxystilbene and nitrohydroxystilbene having different structures, phenolic in the former case, quinonoid in the latter. Whilst

FIG. 2.



I. *Stilbene.*
II. *Nitrostilbene.*
III. *Nitrohydroxystilbene in alcoholic solution.*
IV. ,, ,, *sodium hydroxide.*
V. *Nitromethoxystilbene.*

it may be readily admitted that the structure of a substance containing replaceable hydrogen is the same as that of an alkyl derivative if the two compounds give practically identical absorption spectra, differences in physical properties, whilst suggesting differences of structure, neither prove nor disprove that such exist.

The chemical evidence in favour of a quinonoid transformation is frequently wanting; a difference in chemical behaviour has, however, been observed in the case of alkaline solutions of *p*-nitroaryl-azophenols. Hydroxyazo-compounds usually undergo fission between the two nitrogen atoms of the azo-group when reduced in acid or alkaline solution. Meldola (Trans., 1885, **47**, 659) observed that *p*-nitrobenzeneazophenol is reduced by ammonium sulphide in alkaline solution to *p*-aminobenzeneazophenol, which, being sparingly soluble in alkali, is precipitated, and so protected from further immediate attack. If the linking between the two nitrogen atoms is the same, whether a nitro-group occupy the para-position or not, it is difficult to account for the difference of behaviour towards the same reducing agent.

The greater stability of the C:C linking precludes the observation of such a striking difference in corresponding compounds of the stilbene series, but attention may be drawn to the different behaviour of alkaline solutions of hydroxystilbene and its nitro-derivative towards methyl sulphate as recorded in this paper. If the sodium salt of the latter compound really possesses the structure $NO_2{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}ONa$, the influence of the nitro-group appears inexplicable, for on account of the distance separating it from the ·ONa group, sterical considerations can scarcely come into account.

With a structure such as

$$NaO{\cdot}NO{:}C_6H_4{:}CH{\cdot}CH{:}C_6H_4{:}O,$$

it appeared not impossible that *p*-nitrophenol might be isolated as a result of oxidation with permanganate in alkaline solution; the experiment gave, however, a negative result, the only product isolated being a small quantity of *p*-nitrobenzoic acid. This cannot be taken as an argument in favour of the nitrophenolic structure of the sodium salt, which, being the salt of a very weak acid, is considerably hydrolysed. The *p*-nitrobenzoic acid (identified by the "mixed melting-point" method) is probably produced by oxidation of the hydrolysed nitrohydroxystilbene; it is very stable towards alkaline oxidising agents, whereas all the other possible products are unstable; its isolation is not therefore surprising.

We desire to record our thanks to the Research Fund Committee of the East London College for a grant in aid of this investigation.

East London College,
University of London.

LXXI.—*Nitrites of the Alkylammonium Series. Part IV.* iso*Butyl-, Diethyl-, Dipropyl-, and Tripropylammonium Nitrites.*

By **Prafulla Chandra Rây** and **Jitendra Nath Rakshit**.

The amines used in these preparations were obtained from Kahlbaum, and their purity was tested by their conversion into the respective platinichlorides and estimation of platinum. The nitrites were prepared in the usual manner already described.

iso*Butylammonium Nitrite.*

This compound is a pale yellow, limpid liquid.

Found: $C=39{\cdot}41$; $H=9{\cdot}84$; N(nitritic)$=12{\cdot}06$.

$C_4H_{11}N,HNO_2$ requires $C=40{\cdot}00$; $H=10{\cdot}00$; N(nitritic)$=11{\cdot}66$ per cent.

iso*Butylammonium nitrite* is unstable at the ordinary temperature in the vacuum of the Sprengel air-pump, bubbles of gas being continuously disengaged. The temperature was gradually raised, and finally the decomposition was completed at 100°. The products were nitrogen and minute oily drops of nitrosoamine and butyl alcohol. The quantity of the latter being too small, whether it was the normal alcohol or its isomeride could not be ascertained. At a dilution of 28 litres, the salt was ionised to the extent of 84 per cent.

Diethylammonium Nitrite.

This nitrite can also be obtained by the interaction of mercuric nitrite and diethylamine in aqueous solution; the mercury is precipitated as dimercuriammonium nitrite.* This reaction evidently takes place in accordance with the equation:

$$4NEt_2H_2{\cdot}OH + 2Hg^{II}(NO_2)_2 = NHg_2{}^{II}NO_2 + 3NEt_2H_2{\cdot}NO_2 + 2EtOH + 2H_2O.$$

The alcohol, however, could not be detected in the filtrate, as, when it was subjected to distillation, the diethylammonium nitrite was converted into the nitrosoamine, the penetrating odour of which masks that of iodoform, the latter being formed only in minute quantities.

Diethylammonium nitrite, prepared by the ordinary convenient method, is a pale yellow, crystalline compound; it is much less deliquescent than the ordinary solid substituted ammonium nitrites. It is readily soluble in alcohol, benzene, or chloroform, and sparingly so in ether or carbon disulphide.

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* Whenever mercuric nitrite is treated with ammonia or an alkylamine, the mercury is only partly precipitated; some portion of it invariably remains in the filtrate.

Found: $C=40{\cdot}30$; $H=9{\cdot}64$; $N(\text{nitritic})=10{\cdot}98$.

$C_4H_{11}N,HNO_2$ requires $C=40{\cdot}00$; $H=10{\cdot}00$; $N(\text{nitritic})=11{\cdot}66$ per cent.

This salt is stable at the ordinary temperature (30°), and sublimes when rapidly heated. When slowly heated it decomposes into nitrosodiethylamine, alcohol, and water, the products being similar to those already observed with the analogous methyl derivative.

Dipropylammonium Nitrite.

Dipropylammonium nitrite cannot be obtained by the action of mercuric nitrite on the corresponding amine, the reaction being somewhat complicated; but the ordinary method gives a successful result. It is obtained in slender, lustrous laminæ.

Found: $C=47{\cdot}68$; $H=10{\cdot}30$; $N(\text{nitritic})=9{\cdot}82$.

$C_6H_{15}N,HNO_2$ requires $C=48{\cdot}60$; $H=10{\cdot}80$; $N(\text{nitritic})=9{\cdot}47$ per cent.

The substance is readily soluble in alcohol, chloroform, or benzene, and sparingly so in ether or carbon disulphide. At a dilution of 25 litres, the salt was ionised to the extent of 85 per cent.

Decomposition by Heat.—The salt is stable at the ordinary temperature, and sublimes when heated to 52—60°. The decomposition which occurs evidently takes place as in the case of the lower homologues (Trans., 1911, **99**, 1473). The yield of nitrogen is, however, much larger, proving that the decomposition according to the equation:

$$N(C_3H_7)_2H_2{\cdot}NO_2=2C_3H_7{\cdot}OH+N_2$$

is proportionately greater.

Tripropylammonium Nitrite.

Tripropylamine gives a precipitate of mercuric oxide with mercuric nitrite; consequently the corresponding amine nitrite can be obtained by this method. It is, however, conveniently prepared by the usual method of double decomposition. It is remarkable that trimethyl- and triethyl-ammonium nitrites are solid compounds, whereas tripropylammonium nitrite is a liquid. Three different samples were prepared, but in each case similar results were obtained.

Found: C=56·78; H=11·80; N(nitritic)=8·18.

$C_9H_{21}N,HNO_2$ requires C=56·84; H=11·58;
N(nitritic)=7·53 per cent.

The substance is a pale yellow liquid, possessing the peculiar odour of amine nitrites. It is unstable in a vacuum; at 55—60° the decomposition becomes fairly rapid; the products of decomposition are nitric oxide, tripropylamine, and tripropylammonium nitrate, as in the case of trimethylammonium nitrite (Trans., 1911, **99**, 1474). At a dilution of 20 litres, the salt was ionised to the extent of 60 per cent.

General Survey of the Group.

Having described fifteen members of the series, we are now fairly justified in attempting a general survey of the group. Unfortunately, no simple generalisation is possible, as the chemical and physical properties of the individual members are of an anomalous character; thus, the first member of the series, methylammonium nitrite, is a crystalline solid, whilst the higher homologues, contrary to our expectations, have been found to be pale yellow, viscid liquids. Coming to the secondary amine nitrites, we find that whilst dimethylammonium nitrite, again, is a pale yellow liquid, its higher homologues are, as might be expected, crystalline solids. The anomalous behaviour is also sharply noticeable among the members of the tertiary amine nitrites. Trimethyl- and triethylammonium nitrites are crystalline, but the next higher homologue is a liquid. In their chemical behaviour, however, the first and last agree, as they decompose exactly in the manner of a typical alkali nitrite. The intermediate member, however, triethylammonium nitrite, stands by itself, as it can be sublimed in a vacuum and decomposes in quite a different manner, yielding alcohol, nitrogen, and nitrous and nitric oxides.

Not a single member of the primary alkylammonium nitrites has been found to be capable of sublimation. Benzylammonium nitrite may be taken as an exception; but it has been pointed out that the introduction of a heavy aryl radicle in the molecule favours this condition (Trans., 1911, **99**, 1475). Among the secondary alkylammonium nitrites, dimethylammonium nitrite, the first member of the series, may be taken as an aberrant type so far as its physical properties go, but its immediate higher homologues are solids, and can be sublimed without decomposition; evidently, the latter, being loaded with comparatively heavier radicles, have acquired this property.

No less striking is the marked difference in the properties of the mixed secondary alkylarylammonium nitrites. Benzylmethylammonium nitrite is obtained only in solution, but it undergoes rapid transformation into the nitroso-compound, whilst its higher homologue, benzylethylammonium nitrite, is fairly stable, and can be sublimed.*

Attention may also be drawn to the fact that although the primary amine nitrites readily decompose according to the well-known equation, yielding nitrogen and alcohol, a by-product in small quantities is almost invariably formed in the shape of a nitroso-compound. Secondary amine nitrites, although they undergo ready transformation into the corresponding nitroso-compounds, also yield as by-products nitrogen and alcohol. The formation of alcohol as a decomposition product of triethylammonium nitrite is equally noteworthy.

It may not be out of place here to conclude our investigation of the present series with a brief historical retrospect. Linnemann had prepared propylammonium nitrite in solution by the same method as we have adopted, but as he was investigating the transformation of normal alcohols into their isomerides (*Annalen*, 1872, **161**, 46) he evidently did not have his attention directed towards the isolation of this class of compounds. The preparation of ethyl amino-acetate nitrite, the parent substance of ethyl diazoacetate, by Curtius in 1883, marks the next step in advance, inasmuch as it is the isolation of a real nitrite of an amino-compound. Bamberger has shown that the alicyclic hydrogenated bases, for example, naphthylamine, can form stable nitrites (*Ber.*, 1889, **22**, 771). Wallach has described a series of stable nitrites of the primary and the secondary amines of the terpene group, for example, bornylamine nitrite and dibornylamine nitrite (*Annalen*, 1892, **269**, 257). Noyes has attempted the preparation of a few nitrites of carbinamine, and these were obtained only in solution, but could not be isolated in the solid state (*Amer. Chem. J.*, 1893, **15**, 589). The nitrites of the amidine bases, for example, succinimidine, guanidine, etc., also come under this category, as their bases contain both the amino- and imino-groups; indeed, Lossen was the first to obtain these compounds, and he points out that compounds containing the amino-group, when treated with nitrous acid, had been previously supposed invariably to give rise to the corresponding hydroxy-compounds, and those containing the imino-group under similar conditions to furnish nitroso-derivatives (*Annalen*, 1891, **265**, 170).

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* The strength of these bases as measured by their electrical conductivity does not throw much light on the stability of their nitrites. Thus, ammonia, which is four times weaker than a primary amine, yields a nitrite, which has been found to be far more stable than any alkylammonium nitrite. Again, a secondary alkylamine, which, on an average, is one and a-half to two times stronger than a primary amine, does not necessarily give a more stable nitrite. A tertiary amine, on an average, is only one half as strong as a secondary amine; but the tertiary amine nitrites have been found to be as stable as, if not more stable than, a secondary amine nitrite: $NH_4{\cdot}OH$, $K=0{\cdot}0023$; $NEtH_3{\cdot}OH$, $K=0{\cdot}056$; $NEt_2H_2{\cdot}OH$, $K=0{\cdot}126$; $NEt_3H{\cdot}OH$, $K=0{\cdot}064$ (Bredig, *Zeitsch. physikal. Chem.*, 1894, **13**, 294).

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LXXII.—*Nitrites of the Mercurialkyl- and Mercurialkylaryl-ammonium Series.*

By Prafulla Chandra Rây, Jitendra Nath Rakshit, and Rasik Lal Datta.

It has already been mentioned that the investigation of the interaction of mercuric nitrite and the alkylamines was primarily undertaken with a view to ascertain if the nitrite analogues of the haloid mercury derivatives of the substituted ammonias could be obtained (Trans., 1911, **99**, 1972). The preparation of the first member of the series, trimercuridiethylammonium nitrite, suggested further work on other alkyl substituted compounds, and incidentally this study has afforded an opportunity of gaining an insight into the constitution of mercuriammonium bases.

At the outset it may be laid down as a rule of general application that any amine which with mercuric nitrite gives a substituted compound also necessarily yields in the filtrate a corresponding amine nitrite, including those of the weakest bases, like aniline and toluidine, although the latter undergo decomposition during concentration. The converse, however, does not always hold good; for instance, secondary amines of the purely aliphatic series, for example, dimethyl-, diethyl-, and dipropyl-amines, have not been found to give the corresponding substituted mercury nitrites; but secondary mixed amines with alkylaryl radicles have yielded the expected result (compare Nos. VII and VIII).

The question of the constitution of the so-called infusible white precipitate has given rise to much controversy. One of us has supported the view (*Zeitsch. anorg. Chem.*, 1902, **33**, 193) that this compound may be regarded, not as a double salt as formulated by Rammelsberg (NHg_2Cl,NH_4Cl), but simply with half the molecular weight as mercuriammonium chloride, $NHg^{II}H_2Cl$; and the fact that an analogous compound derived from ethylamine has the simple formula NHEtHgCl has also been adduced in favour of the latter view. The nitrite and its several haloid derivatives have also been referred to the type of dimercuriammonium compounds (NHg_2^{II}) (Trans., 1902, **81**, 645). Of the eleven nitrites which form the subject matter of the present communication, only Nos. I and II can, however, be placed under this category. The remaining nine may be classed as additive compounds of mercuric nitrite with substituted ammonias, including alicyclic bases. It will also be noticed that mercuric nitrite sometimes combines with one molecule of the base and sometimes with two; in fact, a striking analogy is found to exist between this series and the corresponding compounds with mercuric chloride, as described by Pesci (*Zeitsch. anorg. Chem.*, 1897, **15**, 225), the latter being termed by Franklin as mercuric chloride "with amine, pyridine, and quinoline of crystallisation" (*J. Amer. Chem. Soc.*, 1907, **29**, 35). Mercuric nitrite has been found to be the exact analogue of the chloride in this respect.

It is noteworthy that whilst butylamine gives a salt of the type $N_2Hg_3(C_4H_9)_2(NO_2)_2$, its isomeride simply gives an additive compound (No. III). We have not been successful in preparing any substituted compound with propylamine, dimercuriammonium nitrite being invariably obtained. In view of the remarkable family likeness which obtains throughout the haloid and nitrite series of the mercuriammonium bases, it may be pointed out that the hydrated salts, for example, $NHg_2NO_2,\frac{1}{2}H_2O$; $NHg_2Cl,\frac{1}{2}H_2O$; and $NHg_2Br,\frac{1}{2}H_2O$ (Rây, Trans., 1902, **81**, 647), as also Nos. II and III, are not to be looked on as hydroxy-compounds, as Franklin is inclined to do (*loc. cit.*, p. 63). Both mercuric chloride and nitrite,* unlike mercuric nitrate, are very feebly ionised in solution, and hence none of them yields with sodium sulphate the basic sulphate known as "turpeth mineral." In fact, the halide and nitrite derivatives have to be sharply differentiated from the salts of Millon's base.

EXPERIMENTAL.

For convenience of reference the salts described below have been numbered *seriatim*, the first member of the series, trimercuridiethylammonium nitrite, being named No. I.

II. *Trimercuridibutylammonium Nitrite*, $NHg_3(C_4H_9)_2(NO_2)_2,H_2O$.

Trimercuridibutylammonium nitrite was prepared by the same method as used in preparing its lower homologue (Rây and

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* A paper on the ionisation of mercuric nitrite, as based on conductivity, will shortly be communicated.

Rakshit, Trans., 1911, **99**, 1972). It is a white powder, and can be dried at 100° without decomposition.

Found: Hg=69·21; C=11·15; N=6·99.

$C_8H_{18}NHg_3(NO_2)_2,H_2O$ requires Hg=70·42; C=11·26; N=6·57 per cent.

III. *Mercuriisobutylammonium Nitrite*, $C_4H_9{\cdot}NH_2,Hg(NO_2)_2,H_2O$.

This compound is obtained as a dirty white powder. It is appreciably soluble in water; during washing nearly one-third of it passed into solution. It was dried at 100°.

Found: Hg=52·57; C=11·88; N=11·18.

$C_4H_{11}N,Hg(NO_2)_2,H_2O$ requires Hg=52·22; C=12·28; N=10·97 per cent.

IV. *Mercuribenzylammonium Nitrite*,
$C_6H_5{\cdot}CH_2{\cdot}NH_2,Hg(NO_2)_2,H_2O$.

This is obtained as a white precipitate by adding excess of benzylamine to the nitrite solution. The precipitate was washed carefully to free it from adhering sodium nitrite, and finally dried in the steam-oven.

Found: Hg=48·65; C=20·76; N=9·46.

$C_7H_9N,Hg(NO_2)_2,H_2O$ requires Hg=48·00; C=20·14; N=10·07 per cent.

The substance decomposes at 150—160°, giving mercury, mercuric oxide, benzaldehyde, a nitroso-compound, nitric oxide, and nitrogen.

V. *Mercuridiphenylammonium Nitrite*,
$2C_6H_5{\cdot}NH_2,Hg(NO_2)_2,H_2O$.

Mercuridiphenylammonium nitrite is obtained as a pale yellow, crystalline precipitate when a saturated solution of aniline is added to sodium mercuric nitrite. The colour of the substance slightly deepens on drying. It decomposes below 100°; consequently it was dried in a vacuum over sulphuric acid. The crystals are unctuous to the touch.

Found: Hg=41·05; C=29·02; N=11·07.

$C_{12}H_{14}N_2,Hg(NO_2)_2,H_2O$ requires Hg=40·32; C=29·03; N=11·29 per cent.

VI. *Mercuridi*-p-*tolylammonium Nitrite*, $2C_6H_4Me\cdot NH_2,Hg(NO_2)_2,H_2O$.

Mercuridi-p-*tolylammonium nitrite* was prepared similarly to the above, only the solution of *p*-toluidine had to be effected with warm water. It resembles in property the preceding compound.

Found: Hg = 39·57; C = 32·18; N = 10·16.

$C_{14}H_{16}N_2,Hg(NO_2)_2,H_2O$ requires Hg = 38·16; C = 32·06; N = 10·68 per cent.

VII. *Mercuridibenzylmethylammonium Nitrite*, $2C_6H_5\cdot CH_2\cdot NHMe,Hg(NO_2)_2$.

When a solution of benzylmethylamine is added to sodium mercuric nitrite, a white cloudiness immediately appears. After some time a viscous oil collects, which soon solidifies to a mass of crystals.

Found: Hg = 37·42; C = 35·12; N = 10·91.

$C_{16}H_{22}N_2,Hg(NO_2)_2$ requires Hg = 38·02; C = 36·05; N = 10·64 per cent.

VIII. *Mercuridibenzylethylammonium Nitrite*, $2C_6H_5\cdot CH_2\cdot NHEt,Hg(NO_2)_2$.

This was obtained as usual by adding a solution or rather an aqueous emulsion of benzylethylamine to sodium mercuric nitrite. Like the preceding member, it passed through the intermediate stage of an oil. It was obtained as a white mass, which was dried at 100°.

Found: Hg = 35·06; C = 36·61; N = 10·42.

$C_{18}H_{26}N_2,Hg(NO_2)_2$ requires Hg = 35·59; C = 38·43; N = 9·96 per cent.

The value found for nitrogen is a little high, whereas that for the carbon is a little too low; this is accounted for by the oily liquid entangling the mother liquor, rich in sodium nitrite, and crystallising out along with the latter.

IX. *Mercuridipyridinium Nitrite*, $2C_5H_5N,Hg(NO_2)_2$.

To a concentrated solution of mercuric nitrite a concentrated solution of pyridine was added in excess, when a yellow oil immediately separated. The substance crystallises with difficulty, and on being dried loses pyridine; hence it could not be obtained in the pure condition.

Found: Hg = 45·99; C = 23·84; N = 11·79.

$C_{10}H_{10}N_2,Hg(NO_2)_2$ requires Hg = 44·44; C = 26·66; N = 12·44 per cent.

X. *Mercuriquinolinium Nitrite*, $2C_9H_7NH,Hg(NO_2)_2$.

As quinoline is sparingly soluble in water, an aqueous emulsion of it was added to sodium mercuric nitrite as usual, when a yellow oil separated, which, unlike the corresponding pyridine salt, solidified almost immediately. This was collected, washed, and dried in a vacuum over sulphuric acid.

Found: Hg = 34·66; C = 41·21; N = 9·51.

$C_{18}H_{16}N,Hg(NO_2)_2$ requires Hg = 36·1; C = 39·3; N = 10·2 per cent.

The excess in the percentage of carbon is due to a little free quinoline being carried down with the salt, which was precipitated in the oily condition. The percentage of mercury is necessarily low.

XI. *Mercuripiperazinium Nitrite*, $C_4H_{10}N,Hg(NO_2)_2$.

This compound is a white powder, sparingly soluble in water. It was dried at 100°.

Found: Hg = 52·91; C = 12·43; N = 14·50.

$C_4H_{10}N_2,Hg(NO_2)_2$ requires Hg = 52·60; C = 12·69; N = 14·81 per cent.

Attempts to obtain the α-naphthylamine derivative were unsuccessful.

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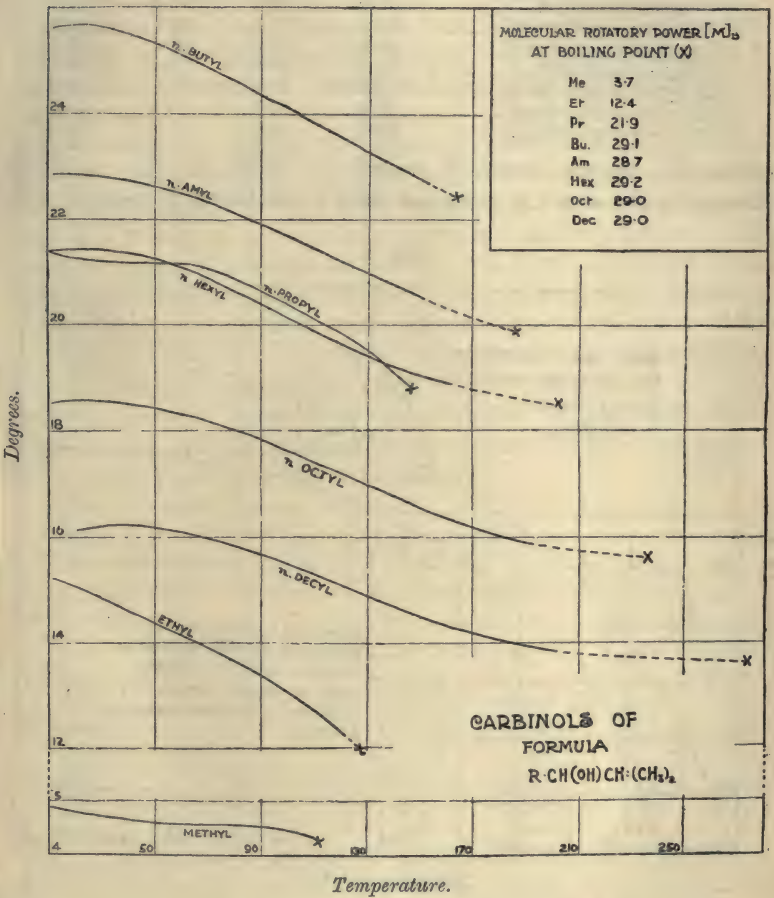
LXXIII.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part II. The Rotations of Some Secondary Alcohols containing the* iso*Propyl Group.*

By Robert Howson Pickard and Joseph Kenyon.

An investigation of the dependence of optical activity on chemical constitution must necessarily take into account the various factors which influence this phenomenon. Of these the least understood, namely, the influences of the solvent and concentration of the solution are eliminated by the consideration only of the rotations of homogeneous liquids. Further, the principal conclusions to be drawn from the authors' previous results (Trans., 1911, **99**, 45) are that (*a*) to eliminate the effect due merely to mass, comparisons of the alteration in rotatory power due to the presence of different groups should be made between series of compounds possessing closely analogous structure, rather than between isolated members of two or more such series; and (*b*) in order to be able to estimate the effect of temperature, which is probably the most disturbing factor in this investigation, such comparisons should be made over a wide range of temperatures, preferably up to the boiling points of the liquids. The disturbing effect, if any, due to the phenomenon of association in these liquids (and up to the present only secondary alcohols have been considered) is probably also eliminated by the consideration of the rotations of series of compounds over wide ranges of temperature, for it is known that association decreases as the temperature increases, and is less in the higher members of an homologous series. It is also necessary to consider the further factor due to the choice of the wave-length of light used for the measurement of the rotations. For the present the authors have themselves used only the sodium flame as a source of light, but determinations by Dr. T. M. Lowry have shown that striking regularities exist in the optical dispersion exhibited by the two series described in this and the former paper (*loc. cit.*). The authors are preparing several such series, and this part of the investigation deals with a series of optically active carbinols of the general formula $R\cdot CH(OH)\cdot CH(CH_3)_2$, where R represents methyl, ethyl, *n*-propyl, *n*-butyl, *n*-amyl, *n*-hexyl, *n*-octyl, and *n*-decyl. The last seven of these, therefore, contain the *iso*propyl group in place of the methyl group present in the corresponding compounds of the series described in Part I. The first three optically inactive carbinols were prepared by Grignard reactions, but as this method is inapplicable beyond the propyl member of this series, the remaining carbinols were obtained by the reduction of the corresponding ketones, which were easily prepared by catalytic decomposition by heated thoria of a mixture of the corresponding acids (Senderens, *Compt. rend.*, 1909, **149**, 995). The resolution of these carbinols into their optically active components has been carried out in much the same manner as that employed for the members of the methyl series, but the recrystallisation of the alkaloidal salts of the carbinyl hydrogen esters (to obtain products of constant rotatory power) has in the case of several of these *iso*propyl compounds proved to be a very tedious and lengthy process. In the case of only three out of the eight members of the series, namely, methyl, *n*-propyl, and *n*-butyl, have both the dextrorotatory and the lævorotatory forms of the carbinols been prepared. Indications, however, were obtained that in the cases of the ethyl, *n*-amyl, *n*-hexyl, and *n*-octyl members of the series the dextrorotatory form of the carbinols could have been obtained also by the recrystallisation of the cinchonidine salts of the hydrogen succinic esters. These salts, however, are very soluble, and on account of the great expenditure of time and material necessary to isolate the active carbinols by this method, experiments in this direction were abandoned when it was discovered that the values for the rotatory powers of the alcohols obtained from the *d*-hydrogen phthalates exhibited the striking regularity mentioned below. The resolutions of these alcohols have been carried out with the same precautions as those laid down in Part I, and that they are approximately (if not absolutely) complete is rendered very probable by the relations exhibited by the rotatory powers, whilst the authors' experience of the methods which have now been applied to some thirty alcohols, also leads them to believe that the resolutions in these cases have been carried to completion. The experimental results of these resolutions, except in the case of methyl*iso*propylcarbinol, differ somewhat from those of the "methyl" series; thus strychnine in each case formed the least soluble salt (*l*B*d*A) with the hydrogen phthalic esters, whilst with brucine complete resolutions are very difficult to effect; in fact, only in the case of the *n*-propyl and *n*-butyl members of the series were the pure brucine salts (*l*B*l*A) of the hydrogen phthalic esters obtained, whereas with each member of the "methyl" series brucine and strychnine each formed the least soluble salt (*l*B*d*A) of the hydrogen phthalate. It is worthy of note that the decyl member of the series contains fourteen carbon atoms, whilst no resolutions were obtained in the case of pentadecan-β-ol and heptadecan-β-ol (compare Proc., 1911, **27**, 312), tridecan-β-ol being the highest member of the "methyl" series obtained in the optically active form. None of these optically active carbinols has been previously described as regards its rotatory power. They are very stable, and can be boiled with alkaline solutions, distilled under the ordinary pressure, and heated with phthalic anhydride without undergoing any racemisation. The specific rotatory powers of these alcohols have been determined at several temperatures up to 200°, or to the boiling points under atmospheric pressure, and are given in table I. By extrapolation of the curves illustrating these results (see Fig. 1), the specific rotatory powers of all the different members of the series at their boiling points have been obtained, and the molecular rotatory powers calculated therefrom. In the case of the higher members, extrapolation has perhaps been carried further than the observations and the experimental errors of the same really warrant, but

FIG. 1.

Specific rotatory powers at different temperatures.



the procedure has been justified to some extent, since the values thus found for the specific rotatory powers at the boiling point lie on a smooth curve.

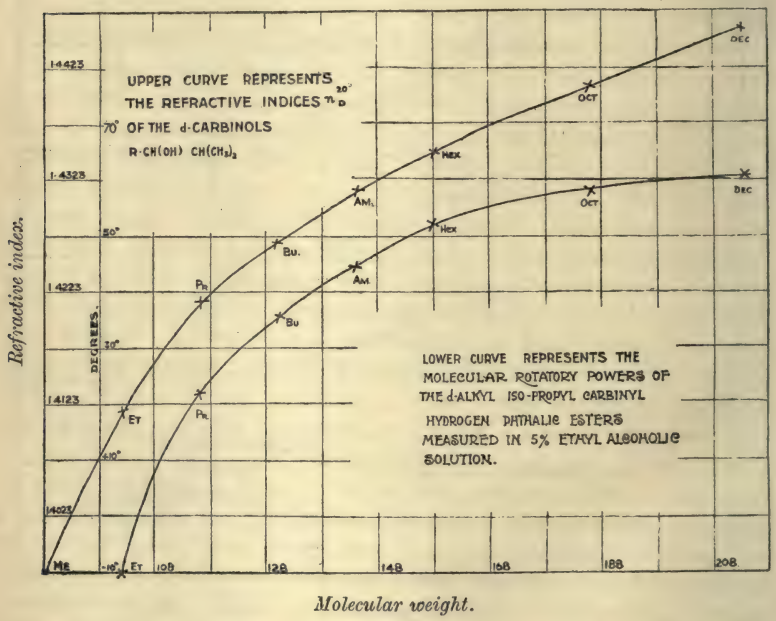
TABLE I.

Specific and Molecular Rotations of the Dextrorotatory Alcohols.

	$[\alpha]^{20}_{D}$.	$[M]^{20}_{D}$.	$[\alpha]^{\text{at b. p.}}_{D}$.	$[M]^{\text{at b. p.}}_{D}$.
*iso*Propylmethylcarbinol	4·85°	4·3°	4·3°	3·7°
*iso*Propylethylcarbinol	15·06	15·4	12·2	12·4
*iso*Propyl-*n*-propylcarbinol	21·25	24·7	18·9	21·9
*iso*Propyl-*n*-butylcarbinol	25·64	33·3	22·4	29·1
*iso*Propyl-*n*-amylcarbinol	22·84	32·9	19·9	28·7
*iso*Propyl-*n*-hexylcarbinol.........	21·46	33·9	18·5	29·2
*iso*Propyl-*n*-octylcarbinol	18·55	34·5	15·6	29·0
*iso*Propyl-*n*-decylcarbinol	16·15	34·5	13·6	29·0

Thus the specific rotatory powers (at 20°) of the carbinols increase as the series is ascended until a maximum is reached with *iso*propyl-*n*-butylcarbinol, when the values decrease in a regular manner to that for *iso*propyl-*n*-decylcarbinol. If, however, the alteration in rotatory power with increase in temperature be measured, a much more striking regularity is brought out, for the molecular rotatory powers of the members of the series *n*-butyl to *n*-decyl [that is, in the series as soon as *R* is of greater mass than that of the *iso*propyl group in $R{\cdot}CH(OH){\cdot}CH(CH_3)_2$] have approximately the constant value $[M]_D$ +29·0° at the boiling point of the

FIG. 2.



liquid. The regularity in the values of the molecular rotation at the boiling point is indicated also by the curves (Fig. 1), which show the alteration of specific rotatory power with the temperature; for the curves for the *iso*propyl-*n*-butyl- to -*n*-decyl-carbinols are obviously very similar, and differ in character from those for methyl- to *n*-propyl-*iso*propylcarbinols.

Attention has been drawn in Part I. to the question of the influence of association on the rotatory powers exhibited by the alcohols there described. Small differences of association are not easy to measure, but from empirical calculations according to various formulæ, such as, for example, that of Longinescu (*Ann. sci. Univ. Jassy*, 1903, **2**, 126), the *iso*propylcarbinols would appear to be associated to a very slight degree only. It may be suggested that the difference 1·5° in the molecular rotatory powers at 20° between *iso*propyl-*n*-butyl- and -*n*-decyl-carbinol is perhaps caused by less association in the carbinol of greater molecular weight.

The regularity exhibited in the values obtained for the molecular rotatory powers of the hydrogen phthalates of the dextrorotatory alcohols, when determined in ethyl alcoholic solution, point to the optical purity of these compounds, whilst the regularity in the value of the refractive indices* of the carbinols points to their purity (see Fig. 2 and tables II and IV).

TABLE II.

Refractive Indices of the Dextrorotatory Alcohols.

	n^{20}_{D}.	$D^{20}_{4°}$.	$\frac{n-1}{d}\cdot M$.	Difference for CH_2.
*iso*Propylmethylcarbinol ...	1·3973	0·8180	42·7	8·2
*iso*Propylethylcarbinol	1·4117	0·8247	50·9	8·4
*iso*Propyl-*n*-propylcarbinol......	1·4215	0·8250	59·3	8·1
*iso*Propyl-*n*-butylcarbinol	1·4265	0·8235	67·4	7·7
*iso*Propyl-*n*-amylcarbinol	1·4314	0 8270	75·1	7·8
*iso*Propyl-*n*-hexylcarbinol	1·4346	0·8290	82·9	7·8
*iso*Propyl-*n*-octylcarbinol	1·4405	0·8327	98·3	7·7
*iso*Propyl-*n*-decylcarbinol	1·4460	0·8390	113·7	

The small break in the regularity of the molecular refraction, which occurs at *iso*propyl-*n*-butylcarbinol, and is caused by the irregular value of its density, coincides with the break in the regularity of the values of the rotatory powers.

The authors are again much indebted to Dr. T. M. Lowry for the determination of the optical dispersion of these alcohols. His determinations, using the ratio α4379/α5461 for the members of the series of carbinols, $CH_3\cdot CH(OH)\cdot R$, described in Part I. (*loc. cit.*), and the series $(CH_3)_2CH\cdot CH(OH)\cdot R$, described in this paper, exhibit remarkable regularities. For, except in the cases of the first members, methylethylcarbinol and methyl*iso*propylcarbinol, approximately constant values have been obtained for each series; thus the value for *d*-methylethylcarbinol is 1·662, and for the other carbinols of the "methyl" series, *d*-methyl-*n*-propyl- to *d*-methyl-*n*-decyl-carbinol, the value approximates to 1·651; whilst *d*-methyl*iso*propylcarbinol gave the value 1·697, and the other members of the "*iso*propyl" series the value 1·663.

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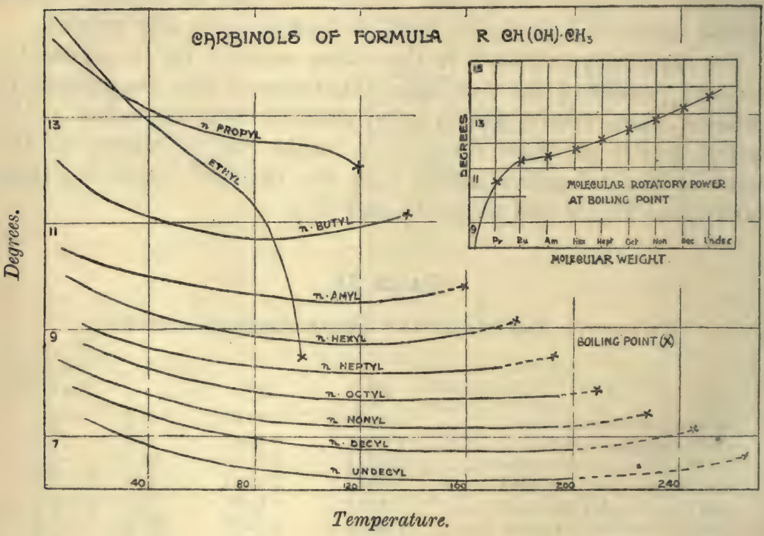
* For the determinations of which we are indebted to Dr. T. M. Lowry.

The contrast of this regularity with the results of the determinations (previously described) of the temperature-coefficients of the specific rotatory power, $[\alpha]_D$, and the derived molecular rotatory power, $[M]_D$, at the boiling point of the carbinols is very striking.

FIG. 3.

Specific rotatory power at different temperatures.



In the "methyl" series all the members (with the exception of methylethylcarbinol) have similar temperature-coefficients of the specific rotatory power, but the molecular rotatory power at the boiling points of the carbinols (see table III, Fig. 3) has apparently not reached a maximum value at methyl-*n*-undecylcarbinol, whilst the corresponding properties of methylethylcarbinol are entirely abnormal. In the "*iso*propyl" series the temperature-coefficients of the specific rotatory power (see Fig. 1) are similar for the carbinols from *iso*propyl-*n*-butyl- to -*n*-decyl-carbinol, and the molecular rotatory powers of these approximate to a constant value at their boiling points. The abnormality in this series therefore extends from methyl*iso*propyl- to *n*-propyl*iso*propyl-carbinol, for the temperature-coefficients of the specific rotatory powers of methyl-, ethyl-, and *n*-propyl-*iso*propylcarbinols differ from one another and also from those of the other members of the series, whilst their molecular rotatory powers at the boiling point have a lower value than the normal one for the series.

Further discussion of these results is reserved until the data to be obtained from the investigation of other similar series are available.

TABLE III.

Molecular Rotatory Powers at the Boiling Points under Atmospheric Pressure.

Alcohol.	Boiling point.	$[M]_D^{\text{at b. p.}}$
Methylethylcarbinol	99°	6·3°
Methyl-*n*-propylcarbinol	118	10·6
Methyl-*n*-butylcarbinol	136	11·3
Methyl-*n*-amylcarbinol	159	11·4
Methyl-*n*-hexylcarbinol	179	11·7
Methyl-*n*-heptylcarbinol............	193	12·1
Methyl-*n*-octylcarbinol	210	12·5
Methyl-*n*-nonylcarbinol	228	12·7
Methyl-*n*-decylcarbinol	245	13·2
Methyl-*n*-undecylcarbinol	265	13·7

The remarks on page 623 relating to the extrapolation to obtain the values for the higher members of the *iso*propyl series apply equally to the above values for the higher members of the methyl series.

Reference may be made to recent papers by E. Fischer, Flateau, Holzapfel, and Gwinner (*Ber.*, 1909, **42**, 2981; *ibid.*, 1912, **45**, 247). These relate to a point in connexion with optical activity, which is now mainly of historical interest only. Guye's hypothesis and his conception of the "product of asymmetry" have been extraordinarily fruitful in provoking a large amount of research in this direction. Many instances will, however, occur to workers in this field, which show that the constitution of the four groups attached to an asymmetric carbon atom has a very great effect on the optical activity of a compound—an effect probably much greater than that of the relative mass of the four groups. The preparation by Fischer and his colleagues of optically active propyl*iso*propylcyanoacetic and butyl*iso*butylacetic acids therefore only serves to emphasise this well known fact, which is also further confirmed by the high specific rotatory power, $[\alpha]_D^{20} \pm 21·25°$, of propyl*iso*propylcarbinol described in this paper.

EXPERIMENTAL.

The Racemic Alcohols.

The first three members of the series were obtained by means of Grignard reactions, the crude products being isolated in the usual manner. The interaction of *iso*propyl bromide and acetaldehyde gave a 37 per cent. yield, and the corresponding chloride a 46 per cent. yield of crude methyl*iso*propylcarbinol, that portion being collected which distilled between 108° and 116°. A similar preparation * from magnesium methyl iodide and *iso*butaldehyde was of no greater purity. The reaction between magnesium ethyl bromide and *iso*butaldehyde gave a 27 per cent. yield of crude ethyl*iso*propylcarbinol boiling between 123° and 132°, whilst the same aldehyde reacting with *n*-propyl bromide gave a 39 per cent. yield of crude *n*-propyl*iso*propylcarbinol boiling between 139° and 144°. Only a very small amount of *iso*propyl-*n*-hexylcarbinol was isolated from the many products of the reaction between *n*-heptaldehyde and magnesium *iso*propyl bromide.

The remaining five members of the series were obtained by the reduction of the corresponding ketones. These were obtained in the manner described in Part I. by the catalytic decomposition (according to Senderens, *Compt. rend.*, 1909, **149**, 995) of mixtures of an excess of *iso*butyric acid with *n*-valeric, *n*-hexoic, *n*-heptoic, *n*-nonoic, and *n*-undecoic acids respectively.

The experimental details were similar to those previously described, except that no glass-wool was mixed with the thorium oxide, as its catalytic properties are considerably diminished by frequent heating with glass-wool.

iso*Propyl* n-*butyl ketone* boils at 159—160°, has D_4^{12} 0·8209, and forms a *semicarbazone*, which crystallises from dilute alcohol in slender, prismatic needles, melting at 111°.

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* In the hope of improving the yield from these reactions, several preparations were made by the very useful modification of carrying out Grignard reactions recently described by Davies and Kipping (Trans., 1911, **99**, 296). This modification consists in allowing an ethereal solution of the aldehyde and alkyl halide to react simultaneously on the magnesium. Now whilst in some cases this method is very convenient, yet for the purpose of this research it was of no advantage, since no small portion of the aldehyde under these conditions is reduced to the corresponding primary alcohol, and it is almost impossible to separate this completely from the secondary alcohol required. This additional by-product of the Grignard reaction is undesirable, whilst the older method does not seem to yield any trace of alcoholic compounds (other than the one required), at least, amongst the by-products of lower boiling point.

iso*Propyl* n-*amyl ketone* boils at 182—184°,* and has D_4^{13} 0·8241.

iso*Propyl* n-*hexyl ketone* boils at 199—201°,* and has D_4^{17} 0·8234.

iso*Propyl* n-*octyl ketone* boils at 232—235°,* and has D_4^{15} 0·8286.

iso*Propyl* n-*decyl ketone* boils at 266—268°/745 mm., and on cooling sets to a mass of waxy leaflets, which melt at 47°.

All these ketones have characteristic odours, reminiscent both of di*iso*propyl ketone and of the normal fatty acid from which they are prepared, whilst the four last do not yield semicarbazones by the usual methods of preparation of these derivatives. In the course of these experiments the following new compounds were isolated:

Di-n-*butyl ketone*, which is a colourless liquid with a pleasant odour, boils at 181—182°, has D_4^{13} 0·8270, and forms a *semicarbazone*, which crystallises from alcohol in glassy, four-sided plates, and melts at 90°.

*Di*iso*propyl ketonesemicarbazone*, which crystallises from dilute alcohol in lustrous plates and melts at 152°.

Di-n-*hexyl ketone*-p-*nitrophenylhydrazone*, which crystallises from alcohol in chocolate-red, prismatic needles, and melts at 97°.

Di-n-*octyl ketone*-p-*nitrophenylhydrazone*, which crystallises from light petroleum in yellow leaflets and melts at 54°.

Di-*n*-hexyl ketone was found to boil at 255°/766 mm., and solidify to a mass of pearly lamellæ, which melt at 33° (compare Kipping, Trans., 1893, **63**, 462).

The *iso*propyl alkyl ketones were then dissolved in moist ether and reduced with finely divided metallic sodium, except in the case of *iso*propyl *n*-decyl ketone, which was reduced in boiling 96 per cent. ethyl-alcoholic solution. The boiling points, under atmospheric pressure, of the carbinols thus obtained were as follows: iso*propyl*-n-*butylcarbinol*, 162°; iso*propyl*-n-*amylcarbinol*, 184°; iso*propyl*-n-*hexylcarbinol*, 200°; iso*propyl*-n-*octylcarbinol*, 236°; iso*propyl*-n-*decylcarbinol*, 274°.

With the exception of the last, these carbinols are very volatile in a current of steam. iso*Propyl*-n-*amylcarbinyl phenylcarbamate* crystallises from light petroleum in hairy needles, and melts at 64°.

The Racemic Hydrogen Phthalic Esters.

The hydrogen phthalic esters of the carbinols were each prepared in the manner detailed in Part I. (*loc. cit.*, p. 58). With the exception of the methyl, *n*-amyl, and *n*-hexyl members, they crystallised readily from light petroleum. The hydrogen phthalate of methyl*iso*propylcarbinol is very soluble in light petroleum, but after removal of the solvent leaves an oil, which soon sets to a crystalline mass. The analogous derivatives of the *n*-amyl- and *n*-hexylcarbinols were obtained as viscous oils, which showed no tendency to crystallise. The purity of each ester was checked by titration in the cold in alcoholic solution with a standard solution of sodium hydroxide. The melting points are given in table IV.

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* At the atmospheric pressure, which was not recorded.

Resolution of the Carbinols.

The resolution of the esters into their optically active components has required more care than the resolution of the corresponding compounds described in Part I.

*Resolution of Methyl*iso*propylcarbinol.*—Equimolecular quantities of the hydrogen phthalate of methyl*iso*propylcarbinol (265 grams) and anhydrous brucine (483 grams) were dissolved in about 1 litre of hot acetone. After concentration to about two-thirds of its bulk, the solution was set aside in the ice-chest for about six hours. The crop of crystals was collected, and repeatedly recrystallised from about the same quantity of solvent. The following details refer to the products of successive crystallisations.

Crystals A.—Weight, 410 grams, softened at 95°, and melted at 131—134°. When heated to 110°, or when exposed to the air for some days, these lost 6·6 per cent. in weight (being probably "acetone of crystallisation").

Crystals B.—Weight, 358 grams. After heating, these melted at 143—145°.

Crystals C were deposited as a hard crust on the bottom of the flask, and the mother liquor was merely drained off.

Crystals D.—Weight, 179 grams. After heating at 110° the melting point was 144—147°, and the specific rotation in anhydrous ethyl alcohol, $[\alpha]_D -5{\cdot}11^\circ$.*

Crystals E.—Weight, 142 grams. Melting point unaltered.

Crystals F.—Weight, 102 grams. After heating at 110°, the melting point was 144—146°, and the specific rotation, $[\alpha]_D -5{\cdot}04^\circ$. The pure brucine salt of the dextrorotatory hydrogen phthalate (102 grams) was dissolved in a small quantity of warm ethyl alcohol, and poured into dilute hydrochloric acid. The ester was extracted with ether, the ethereal extract repeatedly washed with dilute acid to remove any trace of alkaloid, and after removal of the solvent was obtained as a clear, crystalline mass (38 grams) of prisms, which melted out at 44—45°, and had a specific rotation in chloroform of $[\alpha]_D +37{\cdot}87^\circ$.

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* In all cases in this paper where the rotatory power of a compound has been observed in solution, this was prepared by making up an accurately weighed amount (approximately, 1 gram) to 20 c.c. with the solvent.

A repetition of this process with 391 grams of the racemic phthalate gave 36 grams of the dextrorotatory phthalate with $[\alpha]_D + 37{\cdot}95°$ in chloroform. The optically active ester, when dissolved in a cold concentrated aqueous solution of potassium hydroxide, deposits a stable *potassium* salt, which crystallises from acetone, melts at 182—184°, and has $[\alpha]_D + 32{\cdot}46°$ in ethyl alcohol. The ester was hydrolysed in the manner described in Part I., and the optically active alcohol, which is only slightly soluble in water, was extracted with ether and dried with potassium carbonate. *d*-Methyl*iso*propylcarbinol (6 grams) prepared in this way boiled at 110—112°, and in a 1-dcm. tube had $\alpha + 3{\cdot}89°$ at the temperature of the laboratory. The filtrates from the crystals *C*, *D*, *E*, and *F* were decomposed by dilute acid, and yielded 27 grams of the ester with $[\alpha]_D + 26{\cdot}6°$ in chloroform. Similarly, the filtrates from crystals *A* and *B* gave 133 grams of the ester with $[\alpha]_D - 17{\cdot}7°$. This latter ester when hydrolysed gave 38 grams of the carbinol, which had $\alpha_D - 0{\cdot}93°$ in a 50 mm. tube. The ester with $[\alpha]_D + 26{\cdot}6°$ (27 grams) was dissolved in chloroform along with a molecular proportion of strychnine (39·4 grams). When the chloroform had been distilled off, boiling acetone was added to the pasty mass, and 51 grams of the strychnine salt separated out in fine crystals. This was recrystallised in a similar manner six times, and there were then left 7 grams of the salt of the pure dextrorotatory ester, which was, however, contaminated with a little free strychnine. The first lots of crystals melted at 171—173°, and the last at 176—177°; the rotations of the products as obtained during the process varied very irregularly, as they always contained some free alkaloid, that of the purest specimen being $[\alpha]_D - 29{\cdot}4°$ in chloroform. The ester from this salt, obtained in the manner described in Part I. (*loc. cit.*), had $[\alpha]_D + 37{\cdot}9°$ in chloroform. The carbinol, obtained as described above from the first mother liquors from the brucine salt of the hydrogen phthalate, and containing a large proportion of the lævorotatory form, was then converted into the corresponding hydrogen succinate by the method described in Part I. (*loc. cit.*). A warm solution in acetone of this oily hydrogen succinate (59 grams) readily dissolved the equimolecular proportion of brucine (135 grams), and when cooled deposited 105 grams of the brucine salt, which melted at 79—81°. After four recrystallisations from acetone, 38 grams of the salt of the pure lævorotatory ester were obtained of constant melting point (84—86°) and rotation ($[\alpha]_D - 43{\cdot}9°$ in ethyl alcohol). The ester, obtained in the usual manner, was a colourless oil, which, after long keeping in a vacuum, had $[\alpha]_D - 11{\cdot}05°$ in chloroform, and when hydrolysed gave the pure lævorotatory carbinol with $\alpha_D - 0{\cdot}96°$ in a 25 mm. tube.

d-*Ethyl*iso*propylcarbinol.*

The dextrorotatory ethyl*iso*propylcarbinol was isolated from the strychnine salt of the corresponding *d*-hydrogen phthalate, this salt being slightly less soluble in ethyl alcohol than that of the corresponding lævorotatory ester. The salt was prepared by dissolving the components in chloroform, which was afterwards removed as completely as possible by warming on a water-bath, and then dissolving the resulting paste by pouring on to it about twenty times its bulk of warm ethyl alcohol. From this solvent the salt separated in hard, glassy nodules. It was recrystallised by the same procedure, since boiling with ethyl alcohol causes its decomposition with the separation of the free alkaloid. The salt obtained from 562 grams of the ester and 741 grams of strychnine was recrystallised fifteen times, when it was found that the melting point (212°) and the rotation ($[\alpha]_D$ −15·77° in chloroform) of the product (48 grams) were unaltered by further recrystallisation. The mother liquor from the first ten crops of crystals was concentrated, and the crop of crystals obtained was dissolved in the mother liquor from the eleventh crop of crystals in the first series of crystallisations. These were further recrystallised from the twelfth mother liquor, and so on, the crop obtained from the fifteenth mother liquor being recrystallised an additional three times with fresh quantities of solvent. In this way a further 43 grams of the pure salt was obtained. The two lots when decomposed by dilute ammonia yielded 36 grams of the pure *d*-hydrogen phthalate. This set to a hard, crystalline mass, melted at 74—75°, had $[\alpha]_D$ −0·49° in chloroform and $[\alpha]_D$ −4·04° in ethyl alcohol, and when hydrolysed in the usual manner gave *d*-ethyl*iso*propylcarbinol (10 grams). This had a strong camphoraceous odour, boiled at 126° under atmospheric pressure, and had α_D +12·41° in a 1-dcm. tube.

The ester (96 grams) obtained from the first mother liquors in the crystallisation of the strychnine salt was combined with anhydrous brucine (149 grams), and the resulting salt recrystallised several times from acetone. The separation of the salt of the pure lævorotatory ester proceeds very slowly, and was not carried to completion. The least soluble portion of the salt (32 grams) (after seven crystallisations) when decomposed by hydrochloric acid gave an ester, which had $[\alpha]_D$ +1·25° in chloroform and $[\alpha]_D$ +3·05° in ethyl alcohol. The carbinol from this ester boiled at 124—126°, and had α_D −2·35° in a 25 mm. tube.

*Propyl*iso*propylcarbinol.*

The first experiments on the resolution of propyl*iso*propylcarbinol were made on the crystallisation from acetone of the brucine salt of the hydrogen phthalic ester. These were, however, very unsatisfactory, as the rotation of the product obtained after fifteen recrystallisations was still found to undergo alteration when further recrystallised. The resolution was therefore carried out with strychnine in a similar manner to that employed for the resolution of the corresponding ethyl compound; thus, 270 grams of the strychnine salt after ten recrystallisations from alcohol containing traces of chloroform gave 36 grams of the strychnine salt of the pure dextrorotatory ester, whilst a further 8 grams were obtained by working up the last eight mother liquors, followed by six recrystallisations from fresh quantities of solvent. The pure salt melted at 212°, had $[\alpha]_D$ $-19·00°$ in chloroform, and when decomposed by hydrochloric acid yielded the pure *d*-hydrogen phthalic ester of propyl*iso*propylcarbinol, which on evaporation of its ethereal solution left a hard crust of stellate crystals, melted at 79—80°, and had $[\alpha]_D$ $+7·91°$ in chloroform and $[\alpha]_D$ $+8·36°$ in ethyl alcohol. The ester obtained from three other separate sets of recrystallisations had $[\alpha]_D$ $+7·82°$, $+7·71°$, and $+7·85°$ respectively. The carbinol obtained from all these samples of the *d*-ester boiled at 145—146°, and had α_D^{17} $+17·49°$ in a 1-dcm. tube. Although the repeated crystallisation of the brucine salt obtained from the racemic ester (as stated above) did not readily give the salt of the pure *l*-ester, yet on repeating the process with a sample

TABLE IV.

The Hydrogen Phthalic Esters.

			Rotations in			
	Melting point of		Chloroform.		Ethyl alcohol.	
Hydrogen phthalate of	Racemic.	Active.	$[\alpha]_D$.	$[M]_D$.	$[\alpha]_D$.	$[M]_D$.
*iso*Propylmethylcarbinol ...	38—40*	44—45°*	+37·87°	+89·3°	+41·40°	+97·7°
*iso*Propylethylcarbinol ...	69—71	74—75°*	−0·49 †	−1·2	−4·04	−10·1
*iso*Propyl-*n*-propylcarbinol .	59—60	79—80	+7·85	+20·9	+8·36	+22·1
	—	—	−7·82	—	−8·03	—
*iso*Propyl-*n*-butylcarbinol...	47—48	61—62	+13·94	+38·7	+12·78	+35·5
	—	—	−13·80	—	−12·94	—
*iso*Propyl-*n*-amylcarbinol ...	oil	oil	+13·46	+39·3	+15·09	+44·1
*iso*Propyl-*n*-hexylcarbinol ..	oil	49—50	+11·79	+36·1	+17·05	+52·1
*iso*Propyl-*n*-octylcarbinol...	55	47—48	+16·87	+56·3	+17·16	+57·3
*iso*Propyl-*n*-decylcarbinol...	58—59	65—66	+13·90	+50·3	+16·84	+61·0

* Not recrystallised, being very soluble in organic media.

† The hydrogen phthalate of the *d*-carbinol.

of the ester, which was obtained from the first mother liquor remaining from the crystallisation of the strychnine salt, and which already contained 77 per cent. of the *l*-ester, a completely satisfactory result was obtained; thus a mixture of the hydrogen phthalic ester (31·5 grams, with $[\alpha]_D$ $-4·35°$ in chloroform) and brucine (43 grams) after six crystallisations from acetone gave the brucine salt (8·5 grams) of the pure *l*-ester. This salt melted at 136°, had $[\alpha]_D$ $-10·88°$ in ethyl alcohol, and gave the *l*-hydrogen phthalate, with $[\alpha]_D$ $-7·82°$ in chloroform and $[\alpha]_D$ $-8·03°$ in ethyl alcohol.

iso*Propyl*-n-*butylcarbinol.*

The resolution of the hydrogen phthalic ester of *iso*propyl-*n*-butylcarbinol proceeded very smoothly, the pure *d*-ester being obtained by six crystallisations of the strychnine salt from methyl alcohol (or acetone) along with a little chloroform, whilst the pure *l*-ester was readily obtained by seven crystallisations from acetone of the brucine salt. Commencing with 156 grams of the racemic hydrogen phthalate (m. p. 47—48°), there were obtained 46 grams of the *d*-ester with $[\alpha]_D$ $+13·94°$ in chloroform and $[\alpha]_D$ $+12·78°$ in ethyl alcohol, and 20 grams of the *l*-ester with $[\alpha]_D$ $-13·80°$ in chloroform and $[\alpha]_D$ $-12·94°$ in ethyl alcohol. Both of the optically active esters crystallised readily from light petroleum in flat rhombs, which melted at 61—62°, whilst a mixture of the two in approximately equal amounts melted at 48—50°. The *d*-carbinol boiled at 72°/17 mm., and had α_D $+21·04°$ in a 1-dcm. tube; whilst the *l*-carbinol boiled at 87°/36 mm., and had α_D $-21·08°$ in a 1-dcm. tube.

iso*Propyl*-n-*amylcarbinol.*

The separation in any quantity of the strychnine salt of the hydrogen phthalate of *d*-*iso*propyl-*n*-amylcarbinol from the corresponding salt of the lævorotatory ester by fractional crystallisation in ethyl alcohol proved a very tedious process. Boiling with alcohol tends to bring about the decomposition of the salts, so the fractionation was carried out by an extension of the method used for the ethyl member of the series. The chart (Fig. 4) shows the course of a part of the fractional crystallisation, in which one hundred and twenty operations were carried out, commencing with 570 grams of the salts of the two esters. The weights of the fractions numbered M_3, R_6, S_{11}, T_{12} in the chart, and the additional fractions V_{15}, W_{14}, X_{15}, and Y_{18} were 11·0, 8·5, 10·0, 3·0, 1·5, 2·6, 3·5, and 0·8 grams respectively. The melting point of each of these fractions was 181—182°, and they had in chloroform $[\alpha]_D$ varying from $-17·91°$ to $-18·19°$, whereas fraction A, weighing 271 grams, melted at 163—169°, and had $[\alpha]_D - 23{\cdot}33°$ in chloroform. The pure fractions described as above, which amounted in all to 40·9 grams, were then mixed and recrystallised from alcohol, the crop of crystals (33·5 grams) obtained having $[\alpha]_D - 18{\cdot}18°$ in chloroform. These gave the corresponding *d*-hydrogen phthalate (15 grams) as a fairly mobile oil, which did not solidify when kept some time at −15°, and had $[\alpha]_D + 13{\cdot}46°$ in chloroform and $[\alpha]_D + 15{\cdot}09°$ in ethyl alcohol. This ester was hydrolysed in the usual way, but in two stages, (*a*) with a deficiency and the remainder, (*b*) with an excess of potassium hydroxide. The first portion (4·7 grams) of carbinol had $\alpha_D + 9{\cdot}53°$ in a 50 mm. tube, and the second portion (1·7 grams) had $\alpha_D + 4{\cdot}85°$ in a 25 mm. tube. The hydrogen phthalate recovered from filtrate F had $[\alpha]_D - 6{\cdot}6°$ in chloroform, and weighed 80 grams, that from filtrate F_2 had $[\alpha]_D - 3{\cdot}4°$ and weighed 64 grams, and that from filtrate F_3 had $[\alpha]_D - 1{\cdot}0°$ and weighed 8·5 grams, whilst those from filtrates F_4 and F_5 (not shown in the chart) were feebly dextrorotatory and strongly dextrorotatory respectively.

FIG. 4.

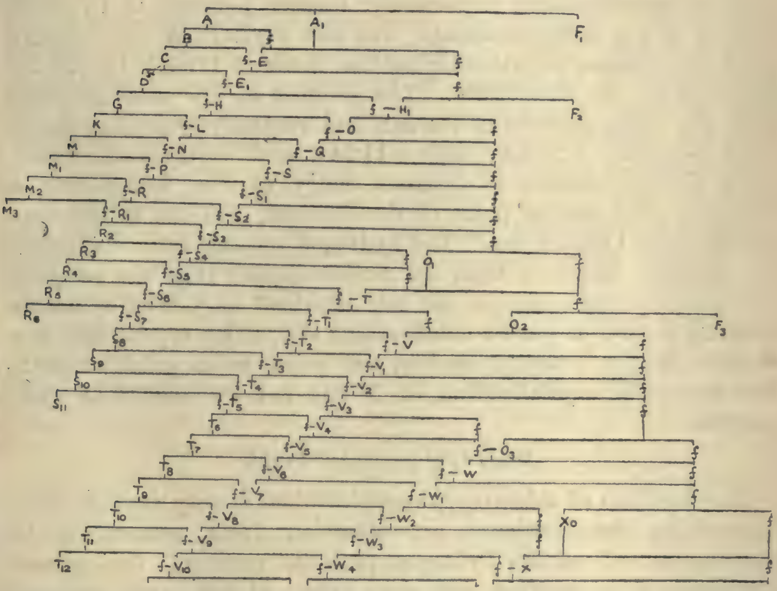

Chart showing the course of a part of the fractionation of the strychnine salts of the hydrogen phthalates of iso*propyl*-n-*amylcarbinol.*

Attempts to obtain the pure lævorotatory carbinol by the fractional crystallisation of the cinchonidine salt of the hydrogen succinic ester were not successful, the salt being so soluble that the process would require too much material.

iso*Propyl*-n-*hexylcarbinol.*

The resolution of the *n*-hexyl member of the series was carried out much in the same manner as that of *iso*propyl-*n*-butylcarbinol. The strychnine salt (568 grams) of the hydrogen phthalic ester was prepared in chloroform, and then recrystallised twice from acetone and afterwards several times from methyl alcohol. After eight crystallisations the pure salt (16 grams) was obtained, and by two series of operations with the mother liquors, involving six and nine further crystallisations respectively, further portions of 16 grams and 17 grams were obtained. The salt crystallises from methyl alcohol in clusters of prismatic needles, melts at 170—171°, and has $[\alpha]_D -22{\cdot}65°$ in chloroform. The samples of the ester obtained from the three portions of the salt had respectively $[\alpha]_D$ in chloroform $+11{\cdot}79°$, $+11{\cdot}83°$, and $+11{\cdot}94°$, and crystallised readily from light petroleum in lustrous, hairy needles, which melt at 49—50°. The boiling point of the carbinol, obtained in the usual manner, was 115°/28 mm. The hydrogen succinic ester made from the carbinol recovered from the mother liquors from the recrystallisation of the strychnine salt was obtained as a mass of needles melting at 26°. It gave a cinchonidine salt, which crystallised from acetone in fine, hair-like needles, but owing to its great solubility the fractional crystallisation of it was not attended with much success.

iso*Propyl*-n-*octylcarbinol.*

The isolation of *d-iso*propyl-*n*-octylcarbinol is very readily accomplished by the fractional crystallisation from acetone of the strychnine salt of the hydrogen phthalic ester of the racemic carbinol. Two hundred and sixty grams of the crude salt gave 12 grams of the pure salt after five crystallisations, and a further 24 grams were readily obtained by working up the mother liquors. The salt of the *d*-ester melts at 174—175°, and has $[\alpha]_D -19{\cdot}9°$ in chloroform. The *d*-ester (18 grams) obtained from this salt (36 grams) solidified in the desiccator to a mass of stellate needles, which melted at 47—48°, and had $[\alpha]_D +16{\cdot}87°$ in chloroform and $[\alpha]_D +17{\cdot}16°$ in ethyl alcohol. The *d*-carbinol (8 grams) obtained from this ester boiled at 135°/26 mm.

iso*Propyl*-n-*decylcarbinol.*

The resolution of this alcohol by means of the fractional crystallisation from acetone of the strychnine salt of the hydrogen phthalic ester proceeded more readily than any of the other resolutions described in this paper. From 52 grams of the racemic ester 14 grams of the pure *d*-ester were obtained; the latter crystallised readily from light petroleum, melted at 65—66°, and had $[\alpha]_D$ +14·15° in chloroform and $[\alpha]_D$ +16·84° in ethyl alcohol. The *d*-carbinol (7 grams) obtained by the hydrolysis of this ester boiled at 164°/29 mm., solidified on cooling to a mass of slender needles which melted at 20°, and was only very slightly volatile in a current of steam.

Determinations of the Density and Rotation of the Dextrorotatory Carbinols.

The following densities have been determined in a pyknometer holding more than 4 c.c., and are compared with water at 4°, and the rotations have been observed in jacketed tubes, 50 mm. and 100 mm. in length, but the figures recorded below have all been calculated for the 100 mm. length. In all cases duplicate observations were made at temperatures below 100° after the alcohol had been heated to the highest temperature recorded; in no case was any difference in rotation observed after the alcohols had cooled after having been heated to the temperatures recorded, thus showing that no racemisation had taken place:

d-*Methyl*iso*propylcarbinol*: $D_{4^\circ}^{15\cdot8^\circ}$ 0·8225, $D_{4^\circ}^{51^\circ}$ 0·7916, $D_{4^\circ}^{71^\circ}$ 0·7722.

Observed rotations: α_D^{5} +4·12°, α_D^{19} +4·02°, $\alpha_D^{28\cdot3}$ +3·80°, $\alpha_D^{40\cdot6}$ +3·70°, $\alpha_D^{64\cdot6}$ +3·52°, α_D^{75} +3·50°, α_D^{86} +3·44°, α_D^{94} +3·36°, α_D^{103} +3·26°.

d-*Ethyl*iso*propylcarbinol*: $D_{4^\circ}^{18^\circ}$ 0·8261, $D_{4^\circ}^{44\cdot5^\circ}$ 0·8035, $D_{4^\circ}^{63^\circ}$ 0·7857.

Observed rotations: α_D^{4} +12·90°, α_D^{12} +12·62°, $\alpha_D^{21\cdot4}$ +12·40°, α_D^{28} +12·16°, $\alpha_D^{32\cdot3}$ +12·02°, α_D^{46} +11·60°, α_D^{65} +11·00°, α_D^{70} +10·82°, $\alpha_D^{80\cdot4}$ +10·52°, $\alpha_D^{89\cdot6}$ +10·16°, α_D^{109} +9·46°, α_D^{112} +9·34°.

d-n-*Propyl*iso*propylcarbinol*: $D_{4^\circ}^{16\cdot7^\circ}$ 0·8266, $D_{4^\circ}^{53\cdot3^\circ}$ 0·7962, $D_{4^\circ}^{74\cdot3^\circ}$ 0·7757.

Observed rotations: $\alpha_D^{4\cdot7}$ +18·06°, α_D^{15} +17·66°, α_D^{29} +17·32°, α_D^{39} +17·10°, $\alpha_D^{54\cdot6}$ +16·80°, α_D^{65} +16·52°, α_D^{71} +16·26°, α_D^{81} +16·14°, α_D^{91} +15·64°, α_D^{95} +15·58°, α_D^{112} +14·88°, α_D^{128} +14·30°, α_D^{147} +13·18°.

d-iso*Propyl*-n-*butylcarbinol*: $D_{4^\circ}^{8^\circ}$ 0·8319, $D_{4^\circ}^{26^\circ}$ 0·8197, $D_{4^\circ}^{50^\circ}$ 0·8005, $D_{4^\circ}^{71\cdot5^\circ}$ 0·7802, $D_{4^\circ}^{96^\circ}$ 0·7569, $D_{4^\circ}^{133^\circ}$ 0·7202, $D_{4^\circ}^{154^\circ}$ 0·6971.

Observed rotations: α_D^{8} +21·24°, α_D^{16} +21·20°, α_D^{37} +20·66°, α_D^{49} +20·26°, α_D^{79} +19·08°, α_D^{108} +17·82°, α_D^{120} +17·20°, α_D^{125} +17·00°, α_D^{132} +16·74°, α_D^{145} +16·16°, α_D^{153} +15·92°.

d-iso*Propyl*-n-*amylcarbinol*: $D_{4^\circ}^{4^\circ}$ 0·8410, $D_{4^\circ}^{17^\circ}$ 0·8323, $D_{4^\circ}^{56^\circ}$ 0·7990, $D_{4^\circ}^{124^\circ}$ 0·7339, $D_{4^\circ}^{150^\circ}$ 0·7084.

Observed rotations: $\alpha_D^{4\cdot5}$ +19·16°, $\alpha_D^{18\cdot5}$ +18·86°, α_D^{46} +18·22°, α_D^{55} +17·94°, $\alpha_D^{75\cdot5}$ +17·10°, α_D^{90} +16·50°, α_D^{110} +16·08°, α_D^{140} +14·96°.

d-iso*Propyl*-n-*hexylcarbinol*: $D_{4^\circ}^{0^\circ}$ 0·8434, $D_{4^\circ}^{15^\circ}$ 0·8333, $D_{4^\circ}^{46^\circ}$ 0·8086, $D_{4^\circ}^{62^\circ}$ 0·7951, $D_{4^\circ}^{113^\circ}$ 0·7509, $D_{4^\circ}^{153^\circ}$ 0·7106.

Observed rotations: α_{D}^{4} +18·02°, α_{D}^{14} +17·90°, $\alpha_{\mathrm{D}}^{29\cdot5}$ +17·60°, $\alpha_{\mathrm{D}}^{45\cdot5}$ +17·20°, α_{D}^{66} +16·58°, $\alpha_{\mathrm{D}}^{83\cdot3}$ +15·94°, α_{D}^{90} +15·72°, $\alpha_{\mathrm{D}}^{113}$ +14·94°, $\alpha_{\mathrm{D}}^{134}$ +14·18°, $\alpha_{\mathrm{D}}^{162}$ +13·40°.

d-iso*Propyl*-n-*octylcarbinol*: $D_{4^\circ}^{0^\circ}$ 0·8458, $D_{4^\circ}^{17^\circ}$ 0·8354, $D_{4^\circ}^{43^\circ}$ 0·8157, $D_{4^\circ}^{69\cdot3^\circ}$ 0·7939, $D_{4^\circ}^{120^\circ}$ 0·7491, $D_{4^\circ}^{145^\circ}$ 0·7268, $D_{4^\circ}^{189^\circ}$ 0·6918.

Observed rotations: $\alpha_{\mathrm{D}}^{3\cdot5}$ +15·60°, $\alpha_{\mathrm{D}}^{17\cdot5}$ +15·46°, $\alpha_{\mathrm{D}}^{27\cdot5}$ +15·32°, α_{D}^{46} +14·90°, $\alpha_{\mathrm{D}}^{60\cdot5}$ +14·64°, α_{D}^{89} +13·46°, $\alpha_{\mathrm{D}}^{124}$ +12·76°, $\alpha_{\mathrm{D}}^{144}$ +12·24°, $\alpha_{\mathrm{D}}^{152}$ +11·92°, $\alpha_{\mathrm{D}}^{179}$ +11·32°, $\alpha_{\mathrm{D}}^{191}$ +10·86°.

d-iso*Propyl*-n-*decylcarbinol*: $D_{4^\circ}^{34^\circ}$ 0·8256, $D_{4^\circ}^{70^\circ}$ 0·7968, $D_{4^\circ}^{91^\circ}$ 0·7800, $D_{4^\circ}^{120^\circ}$ 0·7565, $D_{4^\circ}^{168^\circ}$ 0·7166.

Observed rotations: α_{D}^{19} +13·54°, α_{D}^{32} +13·42°, α_{D}^{39} +13·36°, α_{D}^{54} +12·94°, α_{D}^{90} +12·24°, $\alpha_{\mathrm{D}}^{110}$ +11·64°, $\alpha_{\mathrm{D}}^{123}$ +11·32°, $\alpha_{\mathrm{D}}^{134}$ +11·06°, $\alpha_{\mathrm{D}}^{150}$ +10·64°, $\alpha_{\mathrm{D}}^{167}$ +10·20°, $\alpha_{\mathrm{D}}^{190}$ +9·76°, $\alpha_{\mathrm{D}}^{200}$ +9·56°.

Several additional determinations of the densities and rotatory powers of the alcohols of the series $R\cdot CH(OH)\cdot CH_3$ have been made:

d-Methyl-*n*-propylcarbinol. Observed rotations: $\alpha_{\mathrm{D}}^{104}$ +9·14°, $\alpha_{\mathrm{D}}^{111}$ +9·02°.

d-Methyl-*n*-butylcarbinol: $D_{4^\circ}^{98\cdot5^\circ}$ 0·7444, $D_{4^\circ}^{120^\circ}$ 0·7263.

Observed rotations: $\alpha_{\mathrm{D}}^{100}$ +8·09°, $\alpha_{\mathrm{D}}^{116}$ +8·00°.

d-Methyl-*n*-amylcarbinol: $D_{4^\circ}^{110^\circ}$ 0·7417.

Observed rotations: α_{D}^{97} +7·20°, $\alpha_{\mathrm{D}}^{130}$ +6·98°, $\alpha_{\mathrm{D}}^{148}$ +6·94°.

d-Methyl-*n*-hexylcarbinol: $D_{4^\circ}^{112^\circ}$ 0·7412.

Observed rotations: $\alpha_{\mathrm{D}}^{112}$ +6·53°, $\alpha_{\mathrm{D}}^{145}$ +6·36°, $\alpha_{\mathrm{D}}^{163}$ +6·28°.

d-Methyl-*n*-heptylcarbinol: $D_{4^\circ}^{130^\circ}$ 0·7304.

Observed rotations: $\alpha_{\mathrm{D}}^{113}$ +6·18°, $\alpha_{\mathrm{D}}^{159}$ +5·78°, $\alpha_{\mathrm{D}}^{173}$ +5·76°.

d-Methyl-*n*-octylcarbinol: $D_{4^\circ}^{100^\circ}$ 0·7620, $D_{4^\circ}^{144^\circ}$ 0·7257.

Observed rotations: $\alpha_{\mathrm{D}}^{146}$ +5·64°, $\alpha_{\mathrm{D}}^{153}$ +5·60°, $\alpha_{\mathrm{D}}^{194}$ +5·14°.

d-Methyl-*n*-nonylcarbinol: $D_{4^\circ}^{132^\circ}$ 0·7393.

Observed rotations: $\alpha_{\mathrm{D}}^{108}$ +5·44°, $\alpha_{\mathrm{D}}^{143}$ +5·20°, $\alpha_{\mathrm{D}}^{178}$ +4·98°, $\alpha_{\mathrm{D}}^{193}$ +5·00°.

d-Methyl-*n*-decylcarbinol: $D_{4^\circ}^{123^\circ}$ 0·7512.

Observed rotations: $\alpha_{\mathrm{D}}^{128}$ +5·16°, $\alpha_{\mathrm{D}}^{139}$ +5·02°, $\alpha_{\mathrm{D}}^{169}$ +4·76°, $\alpha_{\mathrm{D}}^{200}$ +4·76°.

d-Methyl-*n*-undecylcarbinol: $D_{4^\circ}^{145^\circ}$ 0·7326.

Observed rotations: $\alpha_{\mathrm{D}}^{112}$ +4·70°, $\alpha_{\mathrm{D}}^{142}$ +4·54°, $\alpha_{\mathrm{D}}^{189}$ +4·24°, $\alpha_{\mathrm{D}}^{197}$ +4·32°.

The authors have much pleasure in acknowledging the able assistance given to them by Mr. John Earnshaw, who has synthesised much of the racemic material for this work, and by Mr. William Osbaldiston, who prepared the racemic *iso*propyl-*n*-decylcarbinol.

Further, the authors desire to express their thanks to the Government Grant Committee of the Royal Society for a grant which has partly defrayed the heavy expenses of this investigation.

Municipal Technical School,
Blackburn.

ANNUAL GENERAL MEETING,

MARCH 25TH, 1912.

Prof. PERCY F. FRANKLAND, LL.D., F.R.S., President,
in the Chair.

Professor A. G. GREEN and Dr. G. SENTER were appointed Scrutators, and the ballot was opened for the election of Officers and Council for the ensuing year.

The Report of the Council on the progress of the Society during the past twelve months was presented by the PRESIDENT; and the TREASURER made a statement as to the Society's Income and Expenditure for 1911. After some remarks with reference to the awarding of Grants from the Research Fund of the Society made by Mr. John Hughes, the Adoption of the Report of the Council, together with the Balance Sheet and Statements of Accounts for the year ended December 31st, 1911, proposed by Professor E. J. MILLS and seconded by Dr. A. HARDEN, was carried unanimously.

A Vote of Thanks to the Auditors was proposed by the TREASURER and seconded by Mr. W. MACNAB.

REPORT OF THE COUNCIL.

On the 31st December, 1910, the number of Fellows was 3,073. During 1911, 136 Fellows were elected, and 2 have been reinstated, the gross total being 3,211. The Society has lost 31 Fellows by death; 37 have resigned; the elections of 3 Fellows have become void; 1 Fellow has been elected an Honorary and Foreign Member, and 35 have been removed for non-payment of annual subscriptions.

The total number of Fellows, therefore, on the 31st December, 1911, was 3,104, showing a net increase of 31 over the preceding year. For the past six years the average number of newly-elected Fellows has been 163, whilst the average increase in membership has been over 60. This year the marked falling off in the number of new Fellows accounts for the small net increase.

The names of the deceased Fellows, with the dates of their election, are:

John Attfield (1862).
Edward Beanes (1864).
Frederic Braby (1869).
Joseph Brown (1882).
Carl von Buch (1877).
Edward Collens (1873).
Albert Cooper (1889).
John Arthur Cunningham (1907).
Stephen Darby (1852).
Richard Hayton Davis (1872).
John Greig Ferrier (1905).
James Forbes (1874).
Albert Harrison (1888).
Alfred Henry Hoit (1904).
William Hudson (1878).
Leonard Parker Kinnicutt (1895).
Frederick Charles Knight (1889).
Isidore Bernadotte Lyon (1873).
William McCowan (1875).
Mervyn Herbert Nevil Story Maskelyne (1851).
John Muter (1870).
Ralph Henry Christopher Nevile (1878).
Temple Augustus Orme (1869).
Lewis Buttle Ross (1870).
Sir Samuel Alexander Sadler (1868).
James Sharp (1885).
Harry Wood Smith (1890).
James Samuel Hourston Walker (1890).
William Whitehouse (1889).
William Williams (1892).
William George Winterson (1908).

The following Fellows have resigned:

Francis Paul Armitage.
William Henry Benson Baker.
George Russell Beardmore.
William Arthur Colebourn.
George Hugh Crisp.
Middleton Henry Dand.
Francis Bridger Dutton.
Walter Nicholas Edwards.
Walter John Elliott.
Bernard Scott Evans.
Joseph Valentine Francies.
John Lawrence van Geyzel.
Archibald Melville Glass.
Herbert Grime.
William Peer Groves.
Archie Cecil Osborn Hann.
Sydney Walters Harris.
John Ansted Harrison.
Arthur Edwin Hill.
Victor George Jackson.
Edwin Charles Jee.
Rudolph Lyon.
William James McKerrow.
Edward Handfield Morton.
Alan Edward Munby.
Cyril Lawrence Norman.
Georges Ponthieu.
Harry James Powell.
James Proude.
James Bertram Russell.
Henry Stanley Shelton.
Charles Joseph Smith.
Brenton Symons.
Harold Munkman Timpany.
Gustave Arthur Troye.
John Watson.
George Edward Welch.

The following Fellow has been elected an Honorary and Foreign Member:

John William Mallet.

The following Fellows have been reinstated by the Council, in accordance with Bye-law IV:

Robert Drysdale MacKechnie.
James Bertram Russell.

The Council will be glad to receive information as to the present address of the following Life Fellows who have not answered the inquiries made in the usual manner: J. Bayne, G. W. Davey, and J. Parkinson.

The question of the misuse of the letters "F.C.S." has again been considered by the Council, and opinion of Counsel has now been received that a person using the letters "F.C.S." without authority and for the purpose of assuming wrongfully the status of a Fellow of the Chemical Society, can be restrained by injunction from so doing.

At the end of 1910 the number of Honorary and Foreign Members was 30. During 1911 the Society has had to mourn the loss of J. H. Van't Hoff, A. Ladenburg, Walthère Spring, and L. J. Troost; whilst on March 2nd E. Bamberger, G. Ciamician, P. H. Ritter von Groth, J. W. Mallet, and W. Nernst were elected. The number of Honorary and Foreign Members at the end of 1911, therefore, was 31.

The Council has great pleasure in offering its hearty congratulations to Mr. Edward Riley, who completed his sixtieth year of Fellowship on December 15th, and to the following, who, during the past year, attained their Jubilee as Fellows:

Major Charles Edward Beadnell, R.A.
Mr. Henry Owen Huskisson.
Mr. Frederick Norrington.

During the year, 342 scientific communications were made to the Society, 265 of which have been published already in the Transactions, and abstracts of all have appeared in the Proceedings.

The volume of Transactions for 1911 contains 2,371 pages, of which 2,270 are occupied by 259 memoirs, the remaining 101 pages being devoted to the Obituary Notices, the Faraday Lecture, the Berthelot Memorial Lecture, the Report of the International Committee on Atomic Weights, the Report of the Annual General Meeting, and the Presidential Address; the volume for the preceding year contains 270 memoirs which occupy 2,601 pages.

The Journal for 1911 contains 5,236 abstracts, which extend to 2,200 pages, whilst the abstracts for 1910 numbered 4,867, and occupied 2,032 pages. The abstracts may be classified as follows:

	Pages.	No. of Abstracts.
Part I.		
Organic Chemistry	1,056	1,785
Part II.		
General and Physical Chemistry		1,097
Inorganic Chemistry		489
Mineralogical Chemistry		136
Physiological Chemistry		717
Chemistry of Vegetable Physiology and Agriculture		343
Analytical Chemistry		669
	1,144	3,451
Total in Parts I. and II.	2,200	5,236

The attention of Authors is drawn to the notice printed on the cover of the Journal regarding extra copies of papers. This notice now reads:

"7. If Authors require more than the 50 reprints allowed by the "Society, they should inform the Editor at the time they send in "their corrected proofs, when the extra copies will be supplied at "rates which can be obtained from the Printers."

The Transactions for 1911 contain obituary notices of Beilstein, Erlenmeyer, Fittig, Landolt, and Menschutkin, accompanied by a portrait of each of these eminent Honorary and Foreign Members. Obituary notices appear, also, of R. Abegg, J. Campbell Brown, Michael Carteighe, O. Guttmann, Sir Walter Palmer, Bart., and C. H. Greville Williams, and the Council expresses its thanks to those gentlemen who have so kindly prepared these notices.

The Faraday Lecture was delivered in the Lecture Theatre of the Royal Institution (by the courtesy of the Managers) on June 14th, by Professor Theodore W. Richards, who took as the subject of his discourse, "The fundamental properties of the elements." The lecture was published in the Transactions for June, and an account of the speeches made at the close of the lecture will be found in the Proceedings (p. 177 *et seq.*).

On November 23rd the Society had the privilege of listening to an account of the life and work of Berthelot from Professor Harold B. Dixon.

Sir Oliver Lodge has kindly consented to deliver the Becquerel Memorial Lecture in the place of Professor Rutherford. The Berthelot and Becquerel Lectures, together with those in honour of Moissan and Cannizzaro, may enable the Council to arrange for the publication of a second volume of Memorial Lectures.

The number of Fellows elected during the early years of the Society's existence has been still further diminished by the death of Nevil Story Maskelyne, elected on June 2nd, 1851, Stephen Darby, elected on November 15th, 1852, and John Attfield, elected on January 16th, 1862. The Society was represented by Sir William Tilden and Professor Crossley at the funeral of Dr. Attfield, and by Dr. Hugo Müller at that of Dr. Nevil Story Maskelyne.

The Council has received a portrait of Dr. John Jeffries presented by Mr. G. H. Gabb, and a portrait of Professor Adolf von Baeyer, presented by the Society of Dyers and Colourists. The best thanks of the Council have been accorded for these gifts, and for a generous bequest of a number of chemical works of historical interest, of which the Library contained no copy, from the family of the late Dr. W. J. Russell.

On the occasion of the Coronation of His Majesty King George V. the Council presented a Loyal Address of Congratulation (Proc., p. 184). The Society co-operated with the other Societies in Burlington House in decorating and illuminating the building during the Coronation festivities.

An address was presented to the Royal Academy of Sciences of Turin on the occasion of the Centenary Commemoration of Amedeo Avogadro (Proc., p. 272). The Society has received from the Academy a copy of the Avogadro Medal which has been placed in the cabinet in the Library.

At the celebration of the 500th Anniversary of the Foundation of the University of St. Andrews, the Society entrusted to Sir William Tilden the presentation of an address of congratulation (Proc., p. 185).

Prof. R. Meldola and Sir William Ramsay have been nominated to represent the Society on the Council of the International Coal Smoke Abatement Exhibition to be held in London in April, 1912, and Prof. J. B. Cohen, Prof. H. B. Dixon, and Prof. A. Smithells attended on behalf of the Society the Conference of the Smoke Abatement League of Great Britain, held in Manchester in November.

The Council desires to record its appreciation of the valuable services rendered to the Society by Professor G. T. Morgan, who, owing to his appointment to the Chair of Chemistry at the Royal College of Science, Dublin, retires from the position of Honorary Secretary, which he has held for two years.

The general invitation to the Society to attend the meetings of the Eighth International Congress of Applied Chemistry to be held in Washington and New York in September, 1912, has been accepted by the Council on behalf of the Society. Further particulars of the Congress will be announced.

The Council considered a suggestion made by Professor Hofmann and Professor Ruff at the request of the German Chemical Society, for the subdivision of the section of Inorganic Chemistry at the Eighth International Congress of Applied Chemistry, and resolved that: "In the opinion of the Council of the Chemical Society, the object of the International Congress of Applied Chemistry is to bring together persons whose interests do not exactly follow the same lines; and they consider that too much subdivision of the various Sections will defeat one of the objects for which the Congress was instituted. The Council, therefore, on general grounds, cannot support the proposal made by Professor Hofmann and Professor Ruff for consideration by the German Chemical Society."

An International Committee has been formed for the purpose of raising a memorial to the late Prof. J. H. van't Hoff, and the Treasurer will be glad to receive donations from Fellows to this fund.

The Longstaff Medal for 1912 has been awarded to Dr. H. Brereton Baker, and the formal presentation of the medal will be made at the Annual General Meeting.

The Council has made a donation of £10 to the International Commission of Publication of Annual Tables of Constants and Numerical Data, Chemical, Physical, and Technological.

During 1911, 1,808 books were borrowed from the Library, as against 1,918 in 1910; of these 419 were issued by post, as compared with 573 in the previous year.

The additions to the Library comprise: 171 books, 104 of which were presented, 438 periodicals (representing 237 Journals), and 87 pamphlets, compared with 163 books, 431 volumes of periodicals (representing 236 Journals), and 141 pamphlets last year.

These figures show a decrease of 110 in the number of books borrowed, and 54 in the number of pamphlets; whilst there is an increase of 8 in the books added, and 7 in the number of periodicals.

With the object of keeping the Library as up-to-date and representative as possible, the Council will especially welcome the gifts of works written by Fellows of the Society.

A year ago attention was called to the fact that the expenditure for 1910 had exceeded the income by £147, but that this could be traced to several causes acting simultaneously.

In spite of the notably smaller number of new Fellows elected and the consequent diminution in receipts from admission fees, the income for the year which has closed exceeds the expenditure by £235 17*s.* 8*d.*, which is more than enough to compensate for the adverse balance of the previous year. The income from all sources for 1911 amounts to £7,735 11*s.* 6*d.*, and the total expenditure to £7,499 13*s.* 10*d.*, the corresponding amounts for 1910 being £7,447 5*s.* 10*d.* and £7,594 12*s.* 2*d.* respectively. Whilst the receipts have thus increased by £288 5*s.* 8*d.*, the expenditure has been reduced by £94 18*s.* 4*d.*, and this has been attained without diminishing in any way the activity and efficiency of the Society.

The Journal is a little smaller in bulk, and has cost about £30 less for printing. Our bill for "corrections" (always a very unsatisfactory and debatable item in our printers' accounts) and the average cost per page for this, grows steadily less owing to the strenuous care of the Editor, aided by the cordial co-operation of the great majority of authors with the Publication Committee and compliance with its suggestions. The exercise of greater care in the preparation of manuscript, the adoption of more concise expression, and the elimination of unnecessary experimental details would very considerably reduce the cost of the Journal, with great advantage to author and reader alike. For 1911 the cost of the Journal was £5,237 13*s.* 7*d.*, as against £5,177 7*s.* 8*d.* for 1910, an increase of only £60 5*s.* 11*d.* Of this, £44 10*s.* 0*d.* is due to an increase in the amount of abstractors' fees, an item paid as "piece work," for which the Society most certainly gets its full value, and the Council takes this opportunity of recording its sense of indebtedness to the abstractors for their important services. In almost all other departments economies have been effected as compared with last year; on other publications about £12, the Library £17, miscellaneous expenses, £8, and administrative expenses £118. These decreases amount in all to £180 17*s.* 5*d.*, and the increases to £85 19*s.* 1*d.*, resulting in the net diminution of expenditure stated above.

The increased profit resulting from the management of the advertisements by the Society's officers has fully justified the changes made in this department more than a year ago, since the net gain to the Society from this source is about £110, as against £75 for

INCOME AND EXPENDITURE ACCOUNT

Income.

		£	s.	d.	£	s.	d.
To Life Compositions					302	0	0
,, Admission Fees					596	0	0
,, Annual Subscriptions—							
Received in advance, on account of 1911		301	0	0			
,, during 1911 ,, 1911		4281	0	0			
,, ,, ,, ,, 1910		374	0	0			
,, ,, ,, ,, 1908–9		7	0	0			
,, ,, ,, Anonymous subscription for 1910		2	0	0			
		4965	0	0			
Less amount included in last year's Income, being valuation of Arrears as per last Balance Sheet		370	0	0			
		4595	0	0			
Add Arrears at date: 1911 £486; 1910 £20; 1909 £6, 1908 £1, estimated to realise as per Balance Sheet		360	0	0			
					4955	0	0
,, Lady Subscribers					4	10	0
,, Investments:—							
Dividends on £6730 Metropolitan Consolidated 3½ per cent. Stock		221	16	4			
,, £1050 London and North Western Railway 3 per cent. Debenture Stock		29	13	2			
,, £1520 14*s.* 3*d.* Cardiff Corporation 3 per cent. Stock		42	19	4			
,, £1400 India 2½ per cent. Stock		32	19	4			
,, £2400 Bristol Corporation 2½ per cent. Debenture Stock		56	10	0			
,, £4341 Midland Railway 2½ per cent. Preference Stock		102	3	10			
,, £1200 Leeds Corporation 3 per cent. Stock		33	18	0			
,, £1500 Transvaal 3 per cent. Guaranteed Stock, 1923/53		42	7	6			
,, £1200 North British Railway 3 per cent. Debenture Stock		33	18	0			
,, £700 Canada 3½ per cent. Stock 1930/50		23	1	6			
,, Income Tax Recovered		30	13	5			
,, Interest on Deposit Account		13	3	1			
					663	3	6
,, Publications:—							
Sales:							
Journals		904	1	11			
Proceedings		30	10	2			
General Index		26	3	0			
Library Catalogue		1	13	3			
Atomic Weight Tables		0	8	3			
Annual Reports on the Progress of Chemistry		152	11	0			
		1115	7	7			
Less Publishers' Commission		106	9	2			
		1008	18	5			
Proceeds of Advertisements in Journal	£184 12 2						
Less Commission	9 16 3						
		174	15	11			
					1183	14	4
,, Sale of Waste-paper, old Ballot Boxes, etc.					3	7	2
,, Subscriptions from other Societies:—							
Society of Chemical Industry		8	8	0			
Society of Public Analysts		10	10	0			
Optical Society		8	8	0			
Optical Convention		0	10	6			
					27	16	6
					£7735	11	6

I have examined the above Accounts with the Books and Vouchers of the Society, and and the Investments.

23, QUEEN VICTORIA STREET,
LONDON, E.C.
13th *March*, 1912

W. B. KEEN,
Chartered Accountant.

FOR THE YEAR ENDED 31ST DECEMBER, 1911.

Expenditure.

	£	s.	d.	£	s	d.
By Expenses on account of Journal and Proceedings:—						
Salary of Editor, including Indexing	570	0	0			
Salary of Sub-Editor	200	0	0			
Editorial Postages	25	9	9			
Abstractors' Fees	529	15	10			
Printing of Journal	2849	6	0			
Illustrations	9	9	10			
Banding	59	13	11			
Printing of Advertisements	65	13	0			
Wrappers and Addressing	122	6	10			
Distribution of Journal	598	4	0			
Authors' Copies	201	10	2			
Insurance of Stock at Clay's	6	4	3			
				5237	13	7
Printing of Proceedings	219	6	3			
Banding ,,	8	11	7			
Distribution ,,	36	17	6			
				264	15	4
,, Annual Reports on the Progress of Chemistry				416	6	8
,, Purchase of back numbers of Journal				3	4	0
,, List of Fellows				69	10	0
,, Faraday Lecture:— Honorarium and Expenses				30	6	6
,, Library Expenses:—						
Salary of Librarian and Assistant	180	16	0			
Books and Periodicals	229	7	1			
Binding	42	3	2			
Bookcases	12	2	0			
				464	8	3
,, Indexing for International Catalogue				30	0	0
,, Coronation Illuminations				10	10	0
,, Portraits of Past Presidents				32	11	0
,, Donation to International Commission for Publication of Physico-Chemical Tables				10	0	0
,, Administrative Expenses:—						
Salary of Assistant Secretary	280	0	0			
Salary of Office Assistant	33	0	4			
Wages (Commissionaire, Housekeeper, and Charwoman)	156	8	0			
Coal and Lighting	37	16	10			
House Expenses and Repairs	86	15	11			
Tea Expenses	28	8	11			
Insurances	11	8	3			
Accountants' Charges	21	0	0			
Commission on Recovery of Income Tax	1	10	8			
Printing	104	3	10			
Stationery	34	10	8			
Illuminated Addresses	8	9	6			
Postages	108	8	9			
Miscellaneous Expenses	18	6	10			
				930	8	6
Balance, being excess of Income over Expenditure, carried to Balance Sheet				235	17	8
				£7735	11	6

certify them to be in accordance therewith. I have also verified the Balance at the Bankers

Approved— FREDERICK B. POWER,
JOHN M. THOMSON,
SAMUEL RIDEAL.

Liabilities.

	£	s.	d.	£	s.	d.
To Subscriptions received in advance				239	0	0
,, Cash received on Account of Annual Reports, Vol. VIII. (not published)				28	7	7
,, Sundry Creditors				1468	17	0
,, Research Fund:—						
As per last Balance Sheet	10505	1	9			
Less Excess of Expenditure over Income for the year	8	12	8			
				10496	9	1
				12232	13	8
,, Chemical Society: Excess of Assets over Liabilities:—						
As per last Balance Sheet...	20157	10	1			
Add Excess of Income over Expenditure for the year	235	17	8			
				20393	7	9
				£32626	1	5

Assets.

	£	s.	d.	£	s.	d.
By Investments (value when acquired):—						
£6730 Metropolitan Consolidated 3½ per cent. Stock	7212	8	6			
£1050 London and North Western Railway 3 per cent. Debenture Stock	839	12	0			
£1520 14*s.* 3*d.* Cardiff Corporation 3 per cent. Stock	1650	0	0			
£1400 India 2½ per cent. Stock	1316	1	0			
£2400 Bristol Corporation 2½ per cent. Debenture Stock	2070	2	0			
£4341 Midland Railway 2½ per cent. Preference Stock	3572	2	5			
£1200 Leeds Corporation 3 per cent. Stock	1143	1	0			
£1500 Transvaal 3 per cent. Guaranteed Stock, 1923/53	1460	13	6			
£1200 North British Railway 3 per cent. Debenture-Stock	1033	11	0			
£700 Canada 3½ per cent Stock, 1930/50	704	8	6			
				21001	19	11
(Estimated present value of Investments, £18301 0*s.* 6*d.*)						
,, Sundry Debtors:—						
Optical Society	1	11	6			
Advertising Accounts	66	16	2			
Messrs. Gurney & Jackson	454	18	3			
Telephone Deposit	1	0	0			
				524	5	11
,, Subscriptions in Arrear, £513. Estimated to realise ..				360	0	0
,, Insurances paid in advance				56	11	4
,, Cash at Bank on Deposit Account	250	0	0			
,, Cash in hand	21	1	5			
	271	1	5			
,, *Less* Overdraft on Current Account	84	6	3			
				186	15	2
,, Research Fund:—						
Investments (value when acquired):						
£1000 North British Railway 4 per cent. No. 1 Preference Stock	1010	0	0			
£4400 Metropolitan Consolidated 3½ per cent. Stock	4587	18	0			
£1034 Great Western Railway 2½ per cent. Debenture Stock	1049	15	11			
£1142 16*s.* New South Wales 3 per cent. Stock ...	1000	0	0			
£1122 Metropolitan Water Board 3 per cent. "B" Stock	1002	16	9			
£1365 Midland Railway 2½ per cent. Debenture Stock	1010	0	9			
£806 Victoria 3 per cent. Stock	706	6	2			
	10366	17	7			
(Estimated present value of Research Fund Investments, £9659 12*s.* 8*d.*)						
,, Cash at Bank	129	11	6			
				10496	9	1
				£32626	1	5

RESEARCH FUND INCOME AND EXPENDITURE ACCOUNT FOR THE YEAR ENDED 31ST DECEMBER, 1911.

Income.

	£	s.	d.	£	s.	d.
To Dividends on:—						
£1000 North British Railway 4 per cent. No. 1 Preference Stock	37	13	4			
£4400 Metropolitan Consolidated 3½ per cent. Stock	145	0	4			
£1034 Great Western Railway 2½ per cent. Debenture Stock	24	6	10			
£1142 16s. New South Wales 3 per cent. Stock...	32	5	10			
£1122 Metropolitan Water Board 3 per cent. "B" Stock	31	14	0			
£1365 Midland Railway 2½ per cent. Debenture Stock	32	2	8			
£806 Victoria 3 per cent. Stock	22	15	4			
				325	18	4
,, Repayments of Research Grants:—						
A. T. Cameron	5	8	7			
H. McCombie	5	0	0			
F. D. Chattaway		1	2			
A. E. Dunstan		12	2			
F. B. Thole		4	6			
G. Dean	5	5	0			
V. H. Veley	5	8	7			
G. Senter		2	6			
A. Clayton	4	4	7			
W. W. Close	5	0	0			
W. Godden	2	9	7			
A. Lapworth	10	0	0			
				43	16	8
,, Income Tax Recovered				20	3	6
,, Balance, being Excess of Expenditure over Income carried to Balance Sheet				8	12	8
				£398	11	2

Expenditure.

	£	s.	d.	£	s.	d.
By Grants to—						
E. C. C. Baly...	10	0	0			
T. Q. Chou	8	0	0			
C. H. Hampshire...	3	0	0			
T. P. Hilditch	10	0	0			
E. Hope	10	0	0			
T. E. Hull	10	0	0			
T. C. James	5	0	0			
J. Kenner	5	0	0			
F. R. Lankshear	12	0	0			
T. M. Lowry	10	0	0			
J. W. McBain	10	0	0			
J. E. Myers	5	0	0			
W. Parry...	10	0	0			
R. Robinson	25	0	0			
R. E. Slade	5	0	0			
Miss I. Smedley	8	0	0			
S. Smith	10	0	0			
F. B. Thole	5	0	0			
H. T. Tizard	8	0	0			
W. E. S. Turner	8	0	0			
D. Tyrer	12	0	0			
O. L. Brady	10	0	0			
Carried forward—	199	0	0			
Brought forward—	199	0	0			
A. T. Cameron	5	0	0			
A. Campion	10	0	0			
D. Cardwell	10	0	0			
F. W. Caton	5	0	0			
F. D. Chattaway	10	0	0			
A. Clayton	10	0	0			
Miss G. Cliffe	5	0	0			
H. M. Dawson	10	0	0			
C. Dorée	5	0	0			
A. C. Dunningham	7	0	0			
J. Ferns	10	0	0			
R. T. Hardman	10	0	0			
E. Hope	15	0	0			
A. Hopwood	10	0	0			
T. E. Hull	12	10	0			
J. W. McDavid	10	0	0			
A. N. Meldrum	5	0	0			
R. S. Pollard	10	0	0			
J. N. Pring	15	0	0			
W. M. Roberts	15	0	0			
D. Segaller	5	0	0			
				393	10	0
,, Commission on Recovery of Income Tax				1	0	2
,, Advertisements				3	13	0
,, Cheque Book					8	0
				£398	11	2

I have examined the above Account with the Books and Vouchers of the Society, and certify it to be in accordance therewith. I have also verified the Balance at the Bankers and the Investments.

W. B. KEEN,
Chartered Accountant,
23, QUEEN VICTORIA STREET,
LONDON, E.C.

18*th March*, 1912.

Approved—
FREDERICK B. POWER,
JOHN M. THOMSON,
SAMUEL RIDEAL.

1910, and £10 in 1909. This is largely due to the energy of Mr. Carr, and to the loyal support given by the Fellows of the Society and other advertisers.

The net income from the investments in the name of the Research Fund amounts to £345 1*s.* 8*d.*, and this, together with returned grants to the extent of £43 16*s.* 8*d.*, made the income available for distribution amongst applicants £388 18*s.* 4*d.*, and as there was a balance in hand, the Council was enabled to distribute a sum of £393 10*s.* 0*d.* in forty-two grants, which varied in amount from £3 to £25.

ADDENDUM.

INTERNATIONAL ASSOCIATION OF CHEMICAL SOCIETIES.

As mentioned in the Proceedings (p. 132 *et seq.*), meetings of the delegates appointed by the French, English, and German Chemical Societies took place in Paris on the 25th and 26th April last, at which the statutes of the Association were drafted, and subsequently ratified by the Councils of the three Chemical Societies responsible for the foundation of the Association. These statutes are printed in full in the Proceedings. They may, however, be briefly summarised as follows:

The object of the Association is to form a bond of union between the several Chemical Societies of the world for the purpose of taking into consideration such matters as are of general and international interest to Chemistry.

All Chemical Societies are eligible to join the Association. The Association is under the direction of a Council consisting of a certain number of members, and each Country can only be represented on the Council by a single Chemical Society, which shall nominate three representatives.

Thus the Council constituted at the Paris Conference consisted of Profs. Béhal, Haller, and Hanriot (French Chemical Society), Profs. Frankland and Meldola, and Sir Wm. Ramsay (Chemical Society), and Profs. Jacobson, Ostwald, and Wichelhaus (German Chemical Society).

The admission of representatives of any Chemical Society is subject to election by a two-thirds majority of the Council.

At the present moment the Council has the following composition:

German Chemical Society:

Prof. W. Ostwald (President of the Association for the ensuing session, 1912), Prof. H. Wichelhaus (Vice-President), Prof. P. Jacobson (General Secretary).

The Chemical Society:
Prof. P. F. Frankland, Prof. R. Meldola (retired),* Prof. Sir Wm. Ramsay.

French Chemical Society:
Prof. Béhal, Prof. Haller, Prof. Hanriot.

Italian Chemical Society:
Prof. G. Carrara, Prof. A. Oglialoro, Prof. E. Paternò.

Russian Chemical Society:
Prof. N. S. Kurnakow, Prof. L. A. Tschugaeff, Prof. P. J. Walden.

American Chemical Society:
Dr. A. L. Day, Prof. W. A. Noyes, Prof. Th. W. Richards.

Swiss Chemical Society:
Prof. F. Fichter, Prof. Ph. A. Guye, Prof. A. Werner.

The following Societies have also joined the Association, but are as yet unrepresented on the Council:

Nederlandsche Chemische Vereeniging.
Polyteknisk Forenings Kemikergruppe (Christiania).
Verein Oesterreichischer Chemiker (Vienna).
Kemisk Forening (Copenhagen).

At the Paris Conference it was resolved that the first work of the Association should be the appointment of Committees in each country, to whom should be entrusted the duty of drafting reports on each of the three subjects:

(*a*) Nomenclature of inorganic chemistry.
(*b*) Nomenclature of organic chemistry.
(*c*) Unification of the methods of notation of physical constants.

The following Committees have been appointed by the Council of the Chemical Society:

Inorganic Nomenclature.	*Organic Nomenclature.*
Sir Wm. Ramsay (Chairman).	Prof. W. P. Wynne (Chairman).
Dr. J. C. Cain.	Dr. J. C. Cain.
Dr. A. Harden.	Prof. F. S. Kipping.

Physical Constants.

Dr. N. T. M. Wilsmore (Chairman).
Dr. J. C. Cain.
Prof. A. Findlay.

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* Prof. Arthur W. Crossley has been appointed by the Council of the Chemical Society to fill the vacancy caused by the retirement of Prof. Meldola.

These Committees, as well as the corresponding ones appointed by the several foreign Chemical Societies, have already sent in reports which will form the subject of discussion by the Council of the Association at their next sessions, commencing on April 11th in Berlin.

A Vote of Thanks to the Treasurer, Hon. Secretaries, Foreign Secretary, and Council for their services during the past year was proposed by Professor H. McLeod, seconded by Mr. S. P. U. Pickering, and acknowledged by Professor J. N. Collie.

In presenting the Longstaff Medal for 1912 to Dr. H. Brereton Baker, the President said:

"Dr. Brereton Baker,—It is my pleasant duty, on behalf of the Society, to make the Presentation of the Longstaff Medal, which has been awarded to you by the Council in recognition of your long-continued, faithful, and brilliant services to Chemical Science.

"Your numerous and remarkable researches on the inactivity of dry gases which culminated in the wonderful discovery that carefully dried oxygen and hydrogen can be heated to the temperature of molten silver without explosion, are of such fundamental importance that an account of them finds a place in the teaching which is imparted even to most elementary students of chemistry, whilst the explanation of your results still baffles all but those who delight in daring speculations.

"You have not, however, restricted yourself to the exploitation of this field in which your skilled labour has turned up so many treasures; but, undaunted by the failure of others, you have directed your attention to the study of the eccentric element tellurium, and have embarked with your great experimental resources on an inquiry into the much-discussed question of its purity. Although in this emprise you have failed to convict tellurium of being contaminated by any subtle attachment, for you have not shaken the accepted atomic weight of this element, yet the undertaking was distinguished by the care, the skill, and the thoroughness which we have learnt to associate with all your work.

"In handing you this medal I would take the opportunity of offering you my personal congratulations, as well as those of the Society, on your recent appointment to the Chair of Chemistry in the Imperial College of Science and Technology, and I would express the earnest hope that you may there, as the successor to Sir William Tilden and to Sir Edward Thorpe, find a congenial atmosphere in which to further prosecute your important researches."

The PRESIDENT then delivered his address, entitled, "Some Stereochemical Problems." Professor R. MELDOLA proposed a vote of thanks to the President, coupled with the request that he would allow his Address to be printed in the Transactions. The motion was seconded by Professor J. J. DOBBIE, and carried with acclamation, the PRESIDENT making acknowledgment.

The Report of the Scrutators was presented, and the PRESIDENT declared that the following had been elected as Officers and Council for the ensuing year:

President: Percy F. Frankland, Ph.D., LL.D., F.R.S.

Vice-Presidents who have filled the Office of President: H. E. Armstrong, Ph.D., LL.D., F.R.S.; A. Crum Brown, D.Sc., LL.D., F.R.S.; Sir William Crookes, O.M., D.Sc., F.R.S.; Sir James Dewar, M.A., LL.D., F.R.S.; Harold B. Dixon, M.A., Ph.D., F.R.S.; A. G. Vernon Harcourt, M.A., D.C.L., F.R.S.; R. Meldola, D.Sc., LL.D., F.R.S.; H. Müller, Ph.D., LL.D., F.R.S.; William Odling, M.A., M.B., F.R.S.; Sir William Ramsay, K.C.B., LL.D., F.R.S.; J. Emerson Reynolds, Sc.D., M.D., F.R.S.; the Rt. Hon. Sir Henry E. Roscoe, LL.D., F.R.S.; Sir Edward Thorpe, C.B., LL.D., F.R.S.; Sir William A. Tilden, D.Sc., F.R.S.

Vice-Presidents: G. T. Beilby, LL.D., F.R.S.; M. O. Forster, D.Sc., Ph.D., F.R.S.; A. Liversidge, LL.D., F.R.S.; E. J. Mills, D.Sc, LL.D., F.R.S.; G. T. Morgan, D.Sc.; W. J. Pope, M.A., F.R.S.

Treasurer: Alexander Scott, M.A., D.Sc., F.R.S.

Secretaries: Arthur W. Crossley, D.Sc., Ph.D., F.R.S.; S. Smiles, D.Sc.

Foreign Secretary: Horace T. Brown, LL.D., F.R.S.

Ordinary Members of Council: W. A. Bone, D.Sc., Ph.D., F.R.S.; W. R. Bousfield, M.A., K.C.; Adrian J. Brown, M.Sc., F.R.S.; H. G. Colman, D.Sc., Ph.D; A. Harden, D.Sc., Ph.D., F.R.S.; A. R. Ling; T. M. Lowry, D.Sc.; A. McKenzie, D.Sc., Ph.D.; H. Marshall, D.Sc., F.R.S.; J. C. Philip, D.Sc., Ph.D.; Sir Boverton Redwood, Bart., D.Sc.; E. J. Russell, D.Sc.

PRESIDENTIAL ADDRESS.

Delivered at the Annual General Meeting, March 25th, 1912.

By Percy Faraday Frankland, Ph.D., LL.D., F.R.S.

Some Stereochemical Problems.

We are passing through a period of centenary celebrations of some of the most important and fundamental discoveries and generalisations in Chemical Science. Nine years ago it was the 100th anniversary of the enunciation of the Atomic Theory by Dalton, five years ago that of the discovery of the alkali metals by Humphry Davy, and again last year was separated by one hundred years from that in which Avogadro formulated his famous hypothesis. I venture to think that of equal significance is the 100th anniversary, which will fall in the year 1915, of the discovery by Biot that certain organic compounds are capable of manifesting optical activity in the liquid and dissolved states. How far-reaching have been the consequences of this observation! The conception of molecular dissymmetry introduced by Pasteur, the arrangement of the atoms in space conceived by Wislicenus and formulated by van't Hoff and Le Bel, together with the whole of the aggressively expanding domain of stereochemistry, one and all trace their descent from this capital discovery of the French physicist. There is, perhaps, no discovery which has enabled the chemist to get at such close quarters with his hypothetical atoms, and none which has served more to increase his belief in their existence and in some of the more salient properties, such as valency, that have been ascribed to them.

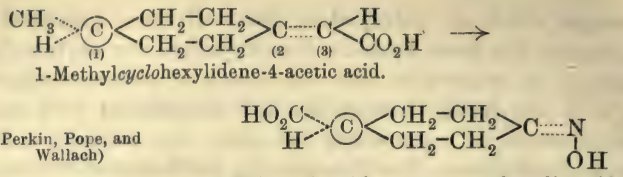
The study of optically active compounds is attracting an ever larger and larger body of enthusiastic workers. When some twenty years ago I first succumbed to the fascination of this subject, the number of British investigators in this field could easily have been counted on the fingers of one hand; at the present time I should find considerable difficulty in even enumerating them at all.

The work on optical activity is at present proceeding in several essentially different directions; thus one group of investigators is engaged in the endeavour to realise new types of asymmetric arrangement which are betrayed by their effect on polarised light. Great progress has been made in this direction, for asymmetry has been induced in connexion with the atoms of elements other than carbon, with the result that we are now acquainted with optically active compounds of *asymmetric nitrogen*, *tin*, *sulphur*, *selenium*, *phosphorus*, and *silicon*. For this striking fulfilment of the doctrines formulated by van't Hoff and Le Bel we are indebted to the beautiful researches of Pope, Peachey, Smiles, Neville, and Kipping, whilst quite recently the long, remarkable, and carefully reasoned investigations of Werner have been crowned by his brilliant achievement in obtaining optically active compounds of asymmetric *chromium* and *cobalt*.

The connexion between optical activity and non-superposable dissymmetry was postulated by Pasteur with reference to the molecule as a whole, and it was only by the subsequent introduction of the principle of valency that the issue could be narrowed down to the asymmetry of individual atoms by van't Hoff and Le Bel.

It was, however, already pointed out by van't Hoff in the first edition (1877) of his classical work on "The Arrangement of the Atoms in Space," that enantiomorphism, and therefore the possibility of optical activity, should be realisable by the allylene types of molecule $R_1R_2C{:}C{:}CR_3R_4$, or in general terms of the type $R_1R_2C{:}C_{2n+1}{:}CR_3R_4$, provided that there is a difference between the groups R_1 and R_2, and also between the groups R_3 and R_4. In such a molecule nevertheless there would appear to be no asymmetric carbon atom.

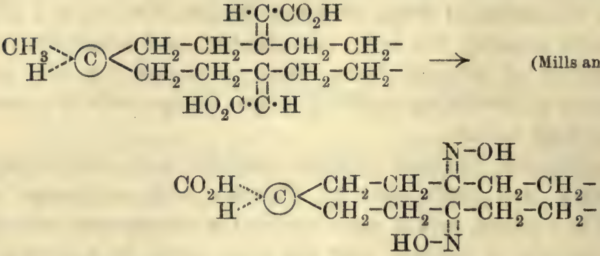
Within the last few years attempts have been made to build up optically active molecules the constitution of which should possess the dissymmetry pertaining to van't Hoff's allylene type, and not containing any asymmetric carbon atom in the commonly accepted sense of the term. Molecules purporting to satisfy these conditions have most ingeniously been conceived, and actually produced, in spite of great experimental difficulties, by Perkin, Pope, and Wallach, as well as by Mills and Bain. Whilst, however, the compounds in question are unquestionably possessed of optical activity, a controversy (Everest, Proc., 1911, **27**, 285) has been raised by Everest and Marsh as to whether one or more of the contained carbon atoms may not legitimately be called asymmetric. The controversy appears to me to be of dialectical rather than scientific interest. The spatial arrangement of these molecules, as well as Everest's contention with regard to them, will be apparent from the following figures:



1-Methyl*cyclo*hexylidene-4-acetic acid.

(Perkin, Pope, and Wallach)

Oxime of *cyclo*hexanone-4-carboxylic acid.



(Mills and Bain)

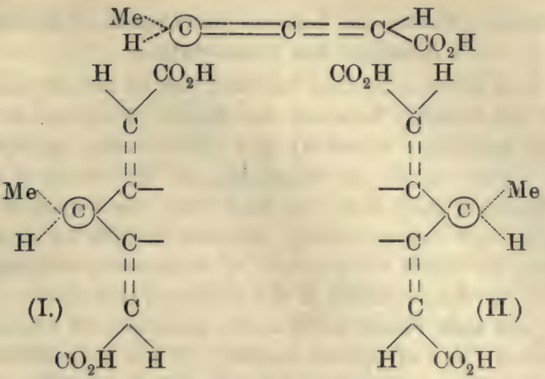
N.B.—The bonds indicated by firm lines are in the plane of the paper, and those marked with dotted lines in a plane at right angles to the paper.

Thus according to Everest (Proc., 1911, **27**, 285) the carbon atom marked (1) in the formula is asymmetric; whilst Marsh (Proc., 1911, **27**, 317) contends that the carbon atoms marked (1), (2), and (3) are all asymmetric, according to his definition (*Phil. Mag.*, 1888) "*that an asymmetric carbon atom is one which, when replaced by its image, gives a formula different from the original formula.*"

It is the contention of Everest that the atoms of carbon, marked Ⓒ, are seen to be asymmetric if the formulæ be dissected, as in the two lower figures, so as to display the four groups to which that carbon atom is by means of its four bonds respectively attached.

There is no question that optical activity can only occur if the molecule as a whole is asymmetric (Pasteur), but it would appear to be a matter of definition only as to whether that molecular asymmetry does not necessarily involve the asymmetry of one or more of the contained atoms. If the dissection of the formulæ as shown above be admitted as legitimate, it is obvious that the atom of carbon Ⓒ is in each case asymmetric according to the ordinary definition, because the dissected formula cannot be superposed on its mirror-image.

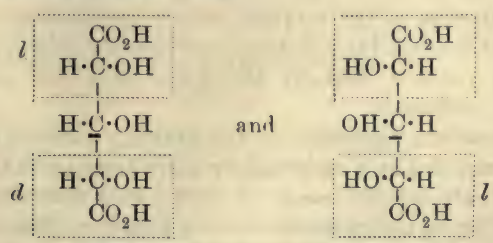
Dissection of a molecule of van't Hoff's allylene type leads to exactly the same relations as are exhibited by the dissection of the above molecules which approximate to this type, thus:



The above dissected formula (I) shows that the arrangement around the carbon atom Ⓒ is asymmetric, as it is not identical with its mirror-image (II).

The dissection in this case is, however, a much more artificial and doubtful procedure than in the former cases, because it involves dealing with the double bond as though it consisted of two ordinary and interequivalent single bonds.

The definition of an asymmetric carbon atom as *one which is attached to four different atoms or groups of atoms* has already led to ambiguity in the case of two enantiomorphous groups being attached to a carbon atom. Two enantiomorphous groups might be regarded as "different," but the facts in connexion with the trihydroxyglutaric acids show that the attachment of two such groups to a carbon atom does not carry the capacity for optical activity, and such a configuration has sometimes been said to possess *pseudo-asymmetry;* thus,



Trihydroxyglutaric acid (inactive form).

are not enantiomorphous, but identical, and the carbon atom marked $\underline{C}$ is not asymmetric, as it might be supposed to be from the usual definition; *thus whilst the ordinary definition of the asymmetric carbon atom may lead to ambiguity, the possibility of optical activity is at once ascertained by an appeal to the symmetry or asymmetry of the molecule as a whole.*

Quantitative Connexion between the Degree of Molecular Rotation and Constitution.

Another line of investigation has had for its object the attempt to trace the relationship between the degree of optical activity (as measured by molecular rotation) and the chemical constitution of compounds. The recent investigations of this nature have undoubtedly received their main impulse from the memorable theory simultaneously and independently proposed in 1890 by Crum Brown and by Guye, in which the *product of asymmetry* was regarded as a measure of the dissymmetry of the molecule as a whole. Although this theory was soon found to be quite incapable of accounting for the ascertained facts of optical activity, it has nevertheless stimulated a large number of workers to renewed endeavours to discover definite relations between chemical constitution and the magnitude of molecular rotation.

Although these investigations have not yet led to any comprehensive generalisation, they have revealed a number of interesting regularities which form in some measure a compensation for the enormous amount of labour that has been bestowed on the subject, which is admittedly one of very great complexity. I will briefly refer to a few of these relations which may be regarded as more or less definitely established.

(1) *Optical Activity in Homologous Series.*—The effect on rotation of ascending an homologous series has been investigated more especially in the case of the homologous esters of an optically active acid or of an optically active alcohol respectively. One of two phenomena is generally observable in the case of such series. *In some series there is a progressive change in the molecular rotation until a maximum has been reached*, and this is followed by a much less marked decline in the rotation, which tends towards a limiting value. *In other series the rotation progressively changes, a limiting value being reached without the appearance of any definite maximum or minimum.*

In either case the maximum or the limiting value of the rotation is generally reached at a surprisingly early term in the series. This is obviously only another mode of saying that alterations made in the constitution of the molecule beyond a certain distance from the asymmetric carbon atom have little or no effect on the molecular rotation.

It is only natural that an explanation should be sought for the reason why the eminently constitutive property of rotation should become so insensitive as the length of an homologous chain is increased beyond a certain limit. Already in 1899 (Trans., 1899, **75**, 368) I ventured to suggest a possible explanation of this phenomenon, in the following terms: "According to the commonly accepted views of stereochemistry, a continuous chain of five carbon atoms will all but return upon itself, and, beyond this, further additions to the chain will lead to such interference as must necessitate a readjustment of the exact positions occupied by the carbon atoms in a shorter chain. It is surely highly probable that this stereochemical change should be betrayed by some irregularity in the rotatory manifestations, for example, by the exhibition of a maximum rotation in those series in which the ascent of the series leads to an increase in the rotatory power." Conversely in those homologous series in which the rotation diminishes with increasing molecular weight the minimum or constant rotation should occur about the term at which the growing chain numbers about five atoms.

In the following tables I have collected the values for the optical activity of a number of homologous series illustrating these phenomena.

A glance at the following homologous series will illustrate the points under discussion:

	$[M]_D^{15°}$.			
	Glycerate.*	Diacetyl-glycerate.†	Dibenzoyl-glycerate.‡	Dimethoxy-propionate.§
Me	−5·76°	−24·56°	+88·20°	−103·8°
Et	12·30	35·56	90·90	114·4
$Pr^α$	19·15	45·17	74·76	122·5
($Pr^β$)	(17·49)	(41·69)	—	—
Butyl	21·37	—	—	124·2
(*iso*Butyl)	(23·05)	(50·38)	—	—
(*sec.*-Amyl)	(24·85)	(50·54)	(70·31)	—
Heptyl	23·05	47·89	—	127·9
Octyl	22·28	47·92	—	125·6

* Frankland and MacGregor (Trans., 1893, **63**, 1430).

† *Ibid.*, 1893, **63**, 1415. ‡ *Ibid.*, 1896, **69**, 104.

§ Frankland and Gebhard (Trans., 1905, **87**, 865).

	$[M]_D^{20°}$.
Menthyl formate	−146·3°
,, acetate	157·3
,, propionate	160·2
,, *n*-butyrate	156·9
,, *n*-valerate	157·3
,, *n*-hexoate	157·7
,, *n*-heptoate	157·7
,, *n*-octoate	155·8

Tschugaeff, *Ber.*, 1898, **31**, 364.

	$[M]_D$.
Amyl formate	+2·33
,, acetate	3·29
,, propionate	3·99
,, *n*-butyrate	4·25
,, *n*-valerate	4·33
,, *n*-hexoate	4·46
,, *n*-heptoate	4·42
,, *n*-octoate	4·49
,, *n*-nonoate	4·44
,, laurate (12)	4·21
,, palmitate (16)	4·17
,, stearate (18)	4·49

Guye and Chavanne, *Compt. rend.*, 1895, **120**, 452; *Bull. Soc. chim.*, 1896, [iii], **15**, 275.

It might at first sight be supposed that if such steric interference were the cause of this limitation, the maximum or constant molecular rotation should always occur at the same term in all homologous series. This, however, is not found to be the case, and it would appear probable that the term at which such interference occurs will depend, not only on the length of what may be called the homologous chain itself, but also on the other groups which are present in the molecule, and which may themselves interfere with the normal development of the homologous chain.

An homologous series in which the development of one of the groups attached to the asymmetric carbon atom might reasonably be supposed to proceed with a minimum of restriction by the other groups is furnished by the admirable investigations of Pickard and Kenyon, who have prepared no less than fourteen active secondary alcohols, of which ten form a continuous series of homologues, thus:

Rotation of Dextrorotatory Alcohols.

Secondary Alcohols (Pickard and Kenyon, Trans., 1911, **99**, 49; this vol., p. 627).

	B. p.	$[M]_D^{20°}$.	$[M]_D^{\text{at b. p.}}$
Methylethylcarbinol	99°	+10·3°	+6·3°
Methyl-*n*-propylcarbinol	118	12·1	10·6
Methyl-*n*-butylcarbinol	136	11·8	11·3
Methyl-*n*-amylcarbinol	159	12·0	11·4
Methyl-*n*-hexylcarbinol	179	12·7	11·7
Methyl-*n*-heptylcarbinol	193	12·9	12·1
Methyl-*n*-octylcarbinol	210	13·7	12·5
Methyl-*n*-nonylcarbinol	228	14·0	12·7
Methyl-*n*-decylcarbinol	245	14·5	13·2
Methyl-*n*-undecylcarbinol	265	14·4	13·7
Methyl*iso*butylcarbinol	—	20·9	—

More recently Pickard and Kenyon have prepared a similar homologous series from *iso*propyl carbinol, and in this it might be anticipated that the *iso*propyl group should give rise to more interference than the methyl group in the previous series. The following figures show that this is actually the case.

I think it also probable that some solvents like alcohol should permit of a more unrestricted development of the rotatory effect of the homologous group than is the case when the same compounds are examined in the liquid condition, and I think that the molecular rotations of the homologous menthyl esters in the liquid state and in alcoholic solution furnish some support to this idea. Some solvents probably produce an opposite effect.

Secondary Alcohols (Pickard and Kenyon, this vol., p. 624).

	$[M]_D^{20°}$.	$[M]_D^{\text{at b. p.}}$
*iso*Propylmethylcarbinol	+ 4·3°	+ 3·7°
*iso*Propylethylcarbinol	15·4	12·4
*iso*Propyl-*n*-propylcarbinol	24·7	21·9
*iso*Propyl-*n*-butylcarbinol	33·3	29·1
*iso*Propyl-*n*-amylcarbinol	32·9	28·7
*iso*Propyl-*n*-hexylcarbinol	33·9	29·2
*iso*Propyl-*n*-octylcarbinol	34·5	29·0
*iso*Propyl-*n*-decylcarbinol	34·5	29·0

(2) *Comparative Rotatory Effects of Saturated and Unsaturated Groupings.*—A very large amount of work has been carried out by a number of investigators with a view to ascertain the relative rotatory effects of saturated and unsaturated groupings.

In this matter there is a general consensus of opinion that *of two similar groupings, the one saturated and the other unsaturated, the latter will have the greater rotatory effect.* A large amount of experimental evidence can be adduced in support of this proposition. It would, however, in my opinion be more correct to say that the presence of unsaturation leads to an *irregularity in the rotatory effect, and not necessarily to an increased rotation.*

The acetylenic union, again, is generally found to have a smaller rotatory effect than the ethylenic, but greater than the saturated, union.

The following table, however, will show that the relations between the rotatory effects of corresponding saturated, ethylenic, and acetylenic groupings are by no means so simple and harmonious as was at first supposed.

*Comparison of Single with Ethylenic and Acetylenic Linkings.**

	$[M]_D^{20°}$		
	β-Phenyl-propionate.	Cinnamate.	Phenyl-propiolate.
l-Amyl	+5·0°	+16·4°	+12·1°
l-Menthyl (10 per cent. benzene)	−178·3	−235·5	−215·9
,, (10 per cent. acetone)	−162·6	−184·3	−157·6
d-Borneol (10 per cent. acetone)	+82·9	+82·6	+89·4
d-Methyl-*n*-hexylcarbinyl	+32·1	+104·4	+131·1
Coniine (4 per cent. chloroform)	−5·1	−20·6	−19·7
Cinchonine (4 per cent. chloroform)	+381·9	+475·2	+511·6

* See Pickard and Kenyon, Trans., 1911, **99**, 46.

Again, the following results (Rupe, *Annalen*, 1903, **327**, 157) show that if the double linking occurs in particular positions with regard to the asymmetric carbon atom, the rotatory effect of the unsaturated may be less than that of the corresponding saturated grouping.

The order of the rotatory effects is:

$$\Delta\alpha\beta > \Delta\beta\gamma > \gamma\delta \text{ and } \delta\epsilon.$$

Nine per cent. Solution in Ethyl Alcohol (Rupe).

	$[M]_D^{20}$.		$[M]_D^{20^\circ}$.
Menthyl $\Delta^{\alpha\beta}$-crotonate	$-203{\cdot}1^\circ$	acetate	$-146{\cdot}1^\circ$
		propionate......	$162{\cdot}5$
		butyrate	$164{\cdot}7$
,, $\Delta^{\alpha\beta}$-pentenate	$-177{\cdot}1$	valerate	$-165{\cdot}7$
,, $\Delta^{\beta\gamma}$-pentenate	$172{\cdot}5$		
,, $\Delta^{\gamma\delta}$-pentenate	$160{\cdot}2$		
,, $\Delta^{\alpha\beta}$-hexenate	$-172{\cdot}4$	hexoate	$-164{\cdot}7$
,, $\Delta^{\beta\gamma}$-hexenate	$164{\cdot}1$		
,, $\Delta^{\gamma\delta}$-hexenate	$153{\cdot}5$		
,, $\Delta^{\delta\epsilon}$-hexenate	$154{\cdot}4$		
,, $\Delta^{\alpha\beta}$-heptenate	$-175{\cdot}5$	heptoate	$-166{\cdot}0$

Very remarkable is the fact, first pointed out by Rupe (*loc. cit.*), that a combination of two pairs of double bonds in the position called "*conjugated*" by Thiele, exercises a very powerful effect on the rotation; thus the menthyl ester of sorbic acid,

$$\mathrm{CH_3}\cdot\underset{\delta}{\mathrm{CH}}:\underset{\gamma}{\mathrm{CH}}\cdot\underset{\beta}{\mathrm{CH}}:\underset{\alpha}{\mathrm{CH}}\cdot\mathrm{CO_2H},$$

has a much higher rotation than the menthyl esters of any of the hexenic acids, thus:

Nine per cent. Ethyl-alcoholic Solution (Rupe).

	$[M]_D^{20^\circ}$.		$[M]_D^{20^\circ}$.
Menthyl sorbate	$-221{\cdot}3^\circ$	Menthyl Δ^1-*cyclo*hexene-carboxylate	$-197{\cdot}0^\circ$
,, $\Delta^{\alpha\beta}$-hexenate ...	$172{\cdot}4$	Menthyl Δ^2-*cyclo*hexene-carboxylate	$156{\cdot}9$
,, $\Delta^{\beta\gamma}$-hexenate ...	$164{\cdot}1$	Menthyl *cyclo*hexane-carboxylate.....................	$157{\cdot}3$
,, $\Delta^{\gamma\delta}$-hexenate ...	$153{\cdot}5$		
,, $\Delta^{\delta\epsilon}$-hexenate ...	$154{\cdot}4$		
,, benzoate	$217{\cdot}2^\circ$		

The different effects in exalting and depressing the rotation according to the position of the double bond is also illustrated by the following compounds:

		$[M]_D^{19^\circ}$.	
	Menthyl allyl ether *.........	$-192{\cdot}5^\circ$	$-\textcircled{C}\cdot\mathrm{O}\cdot\mathrm{CH_2}\cdot\underset{\alpha}{\mathrm{CH}}:\underset{\beta}{\mathrm{CH_2}}$
	,, propyl ether †	$182{\cdot}5$	
		$[M]_D^{20^\circ}$.	
Pyridine solution	Tartaric allylamide ‡	$+251{\cdot}0^\circ$	$-\textcircled{C}\mathrm{HOH}\cdot\mathrm{CO}\cdot\underset{\alpha}{\mathrm{N}}\mathrm{H}\cdot\underset{\beta}{\mathrm{CH_2}}\cdot\underset{\gamma}{\mathrm{CH}}:\underset{\delta}{\mathrm{CH_2}}$
	,, propylamide	$+289{\cdot}0$	
	Malic allylamide §	$-72{\cdot}7$	
	,, propylamide	$-90{\cdot}5$	

* Haller and March (*Compt. rend.*, 1904, **138**, 1665).

† Tschugaeff (*Chem. Centr.*, 1902, **11**, 1238).

‡ Frankland and Twiss (Trans., 1906, **89**, 1854).

§ Frankland and Done (*ibid.*, 1861).

Thus menthyl allyl ether, in which the double bond exalts the rotation, may be regarded as a $\Delta^{\alpha\beta}$-compound, whilst tartaric and malic allylamides, in which the double bond depresses the rotation, may be regarded as a $\Delta\gamma\delta$-compound.

The marked influence of the "conjugated" position on rotatory effect has been greatly emphasised by Hilditch in the course of a number of valuable investigations. The following very extended series of menthyl esters of the homologous dibasic acids is due to Hilditch:

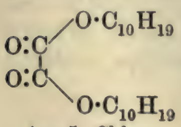
Menthyl Esters of Dibasic Acids. Hilditch (Trans., 1909, **95**, 1581).

Chloroform Solution, $[M]_D^{15°}$.

		$p=5.$	$\div 2.$		$p=2.5.$
Dimenthyl oxalate	(2)	−380·6	(190·3)	(*158·2*)	−378·4
,, malonate.........	(3)	301·1	(150·6)	(*156·6*)	302·6
,, succinate	(4)	322·7	(161·4)	(*161·2*)	324·6
,, glutarate.........	(5)	328·3	(164·2)	(*161·9*)	327·1
,, adipate	(6)	*353·6*	(176·8)	(*164·4*)	*352·8*
,, pimelate	(7)	341·5	(170·8)	|	339·3
,, suberate	(8)	331·1	(165·6)	|	329·8
,, azelate	(9)	*337·2*	(168·6)	|	335·5
,, sebacate	(10)	320·6	(160·3)	|	318·8
,,	(14)			(*156·7*)	
,,	(16)			(*156·8*)	

[Number of carbon atoms in molecule of acid]. [Menthyl esters of fatty acids in chloroform solution (Hilditch)].

Hilditch attributes the extraordinarily high rotation of menthyl oxalate to the presence of the conjugated grouping which it contains. It will be seen from the above table that it has by far the highest rotation of any of the members of the homologous menthyl esters of the dibasic acids.



($p=5$. Chloroform solution.)
$[M]_D^{15°}$ −380·6°.

Very remarkable, again, is the maximum exhibited by this series in the case of dimenthyl adipate, the molecule of which may be regarded as corresponding with two molecules of menthyl hexoate, which possesses the maximum rotation in the series of menthyl esters of the normal fatty acids in chloroform solution, as quite recently determined by Hilditch (this vol., p. 205).

(3) *The* cis- *and* trans-*isomerism of ethylenic compounds* is reflected by their optical activity, as is seen in the case of the amyl esters of fumaric and maleic acids and some of their derivatives (Walden, *Zeitsch. physikal. Chem.*, 1896, **20**, 377), thus:

	$[M]_D$.		$[M]_D$.
Diamyl fumarate.........	+15·17	Diamyl bromofumarate	+20·07
,, maleate	11·82	,, bromomaleate..	15·36
,, chlorofumarate	16·78	,, methylfumarate	16·01
,, chloromaleate..	11·70	,, methylmaleate	11·17

(4) *Comparative Rotatory Effect of Heterogeneous Groupings.*—Very noticeable is the manner in which the mode of combination of the asymmetric carbon (P. Frankland and H. H. O'Sullivan, Trans., 1911, **99**, 2328) with another group affects the rotation much more than differences within limits in the arrangement of the group itself, thus:

	$[M]_D^{19-20^\circ}$.
(1) $C_{10}H_{19}\cdot O\cdot CH_2-\vdots-CO\cdot NH\cdot CH_2\cdot CH{:}CH_2$ .... (Menthoxyacetic allylamide.)	−192·5°
Menthoxyacetic propylamide	−193·7
(2) $C_{10}H_{19}\cdot O\cdot CH_2-\vdots-CH{:}CH_2$ .... (Menthyl allyl ether.)	−192·5
(3) $C_{10}H_{19}\cdot O\cdot CO-\vdots-CH_2\cdot NH\cdot CH_2\cdot CH{:}CH_2$ .... (Menthyl allylaminoacetate.)	−160·5
(4) $C_{10}H_{19}\cdot O\cdot CO-\vdots-CH_2\cdot CH_3$ .... (Menthyl propionate.)	−160·2

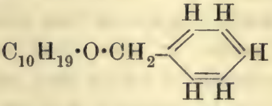
It will be observed that (1) and (3) are isomeric, the menthyl group having the ether attachment in (1) and the ester attachment in (3), whilst the allyl group has the amide attachment in (1) and the amino-attachment in (3).

Again, very striking is the much greater rotatory effect of the menthoxyacetic ester than the menthoxyacetic amide grouping; thus:

$$C_{10}H_{19}\cdot O\cdot CH_2\cdot CO\cdot O\cdot CH_2\cdot CH{:}CH_2.$$

	$[M]_D^{20^\circ}$.
Menthoxyacetic allyl ester	−234·4°
,, propyl ,, ...	234·1

This effect is seen to be quite unconnected with the unsaturation of the allyl radicle, inasmuch as the propyl compound exhibits almost exactly the same molecular rotation. This rotation is almost exactly repeated in the case of



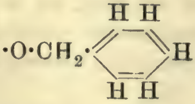
$[M]_D^{20^\circ}$ − 232·7°.

Menthyl benzyl ether.

in which we have the conjugated grouping of the benzene ring. The almost exact equality in rotatory effect of

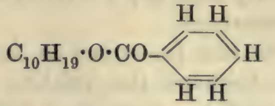
$$\cdot O\cdot CH_2\cdot CO\cdot O\cdot CH_2\cdot CH_2\cdot CH_3$$

and



is very surprising in view of the generally powerful effect of the conjugated grouping. Moreover, the two compounds above mentioned—menthoxyacetic allyl ester and menthoxyacetic propyl ester

—although devoid of any conjugated grouping whatsoever, are nevertheless amongst the most highly active derivatives of menthol; thus even



Menthyl benzoate.

has only $[M]_D^{20^\circ}$ -239°.*

Notwithstanding the apparently capricious nature of the degree of optical activity and the frequent inscrutability of its cause, it may sometimes be possible to predict from analogy with surprising success. Of this I had recently a very remarkable example in the case of menthyl nitrilotriacetate prepared by Mr. Hugh O'Sullivan and myself (this vol., p. 287). This compound,

$$N(CH_2{\cdot}CO{\cdot}O{\cdot}C_{10}H_{19})_3,$$

Menthyl nitrilotriacetate.

may obviously be regarded as a disubstitution derivative of menthyl aminoacetate. Now we had previously shown (Trans., 1911, **99**, 2326) that

		$[M]_D^{20^\circ}$.
Menthyl allylaminoacetate	=	−160·5°
,, propylaminoacetate	=	158·3

and that inasmuch as these molecular rotations are almost identical with those of

		$[M]_D^{20^\circ}$.
Menthyl propionate..................................	=	−160·2°
,, phenylpropionate..............................	=	−161·9
Normal constant of the menthyl homologous fatty esters		157·8

(Tschugaeff, *Ber.*, 1898, **31**, 364.)

it appeared that but little change is effected in the molecular rotation by constitutional changes made in the fatty chain at a point so remote from the asymmetric carbon atoms of the menthyl group. The two complex menthyl acetate groups which are attached to the nitrogen of the menthyl aminoacetate should, therefore, have no material influence on the rotation of that aminoacetate group. The same argument, however, may obviously be applied to each of the three similar groups respectively attached to the nitrogen, and it would be anticipated, therefore, that the molecular rotation of menthyl nitrilotriacetate should be about three times that of the monomenthyl esters mentioned above. As a matter of fact, the relation is:

Menthyl nitrilotriacetate ...... $[M]_D^{19^\circ} = -477{\cdot}1^\circ \div 3 = -159{\cdot}0^\circ$.

---

* Cohen (Trans., 1911, **99**, 1059).

Thus the coincidence is much closer than could reasonably have been anticipated. In the present state of our knowledge, however, such predictions can only be safely hazarded *after* the experimental figures have been ascertained!

(5) *The Effect of Position Isomerism in Aromatic Compounds on Molecular Rotation.*—Perhaps the relation between constitution and rotatory power which has been most fully investigated is that of position isomerism in the aromatic groups present in optically active compounds. This has formed the subject of so many contributions to chemical literature that it would be impossible in the short time at my disposal to review it even in the briefest outlines. This is fortunately the less necessary, as the evidence is on the whole extremely concordant in showing that the rotatory effects of isomeric disubstituted benzene derivatives stand in the order:

$$\text{ortho} < \text{meta} < \text{para.*}$$

A number of years ago, in 1896, I ventured to suggest (Trans., 1896, **69**, 1583) that, for reasons based on the relative position of the centre of gravity of the unsubstituted aromatic nucleus on the one hand, and those of the three isomeric disubstitution derivatives on the other, it was to be anticipated that the order of the rotatory effects should be:

$$\text{ortho} < \text{phenyl} < \text{meta} < \text{para.}$$

The special feature of these theoretical considerations was that they furnished an explanation of the smaller rotatory effect of the *o*-toluyl than that of the benzoyl group, which we had discovered to be the case in the ditoluyl and dibenzoyl tartrates.

Whether the theoretical considerations which postulated this order were sound or unsound, I am not prepared to say, but I do know that the order is almost invariably correct as far as the ortho-grouping having an inferior rotatory effect to the phenyl is concerned, whilst in a considerable number of cases the rotatory value of the phenyl grouping lies between that of the meta- and the para-derivative, and in some the rotatory effect of the phenyl is even greater than that of the para. The number of examples which can be cited in support of this regularity has been greatly multiplied by the interesting researches of Prof. Cohen and his pupils.

I cannot do better than illustrate the validity of my rule by means of the results which Cohen has himself obtained and recorded in a single table in one of his recent communications to the Transactions of our Society (Trans., 1910, **97**, 1737).

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* Goldschmidt and Freund, *Zeitsch. physikal. Chem.*, 1894, **14**, 394; see also Guye and Chavanne, *Bull. Soc. chim.*, 1896, [iii], **15**, 298; Tschugaeff, *Ber.*, 1898, **31**, 1775; Welt, *Ann. Chim. Phys.*, 1895, [vii], **6**, 142; Binz, *Zeitsch. physikal. Chem.*, 1893, **12**, 727; Frankland and McCrae, Trans., 1898, **73**, 307.

Position Isomerism and Optical Activity (Cohen and Dudley, Trans., 1910, **97**, 1737).

	$[M]_D^{20^\circ}$.	$[M]_D^{100^\circ}$.
Menthyl benzoate	−239·0	−232·7
,, *o*-toluate	231·1	223·1
← – – →	←——→	←——→
,, *m*-toluate	240·0	234·7
,, *p*-toluate	246·4	237·2
,, *o*-methoxybenzoate	148·2	154·7
← – – →	←——→	←——→
,, *m*-methoxybenzoate	247·6	242·7
,, *p*-methoxybenzoate	250·7	238·6
,, *o*-ethoxybenzoate	—	157·3
← – – →	←——→	←——→
,, *m*-ethoxybenzoate	244·0	237·4
,, *p*-ethoxybenzoate	—	238·3
,, *o*-propoxybenzoate	170·4	180·1
← – – →	←——→	←——→
,, *m*-propoxybenzoate	240·6	235·1
,, *p*-propoxybenzoate	250·1	234·0
,, *o*-*iso*propoxybenzoate	168·8	175·7
← – – →	←——→	←——→
,, *p*-*iso*propoxybenzoate	246·1	233·3
,, *o*-*iso*amyloxybenzoate	186·8	196·2
← – – →	←——→	←——→
,, *m*-*iso*amyloxybenzoate	240·6	237·6
,, *p*-*iso*amyloxybenzoate	247·6	233·8
,, *o*-allyloxybenzoate	—	174·9
← – – →	←——→	←——→
,, *p*-allyloxybenzoate	251·8	236·9
,, *o*-benzyloxybenzoate	172·3	162·8
← – – →	←——→	←——→
,, *p*-benzyloxybenzoate	255·1	238·9
,, *o*-dimethylaminobenzoate	—	100·9
← – – →		←——→
,, *p*-dimethylaminobenzoate	—	257·9

[N.B.—The arrow ← – – → is placed in the position which the benzoate should occupy according to my rule, and the arrow ←——→ in the position which experimentally it is found to occupy.]

Thus not once in these nine cases is my rule violated in respect of the order ortho<phenyl<meta, whilst the para is slightly out of order with regard to the meta on several occasions. The difference between the rotations of the meta- and para-compound in those cases is, however, so slight that too much importance must not be attributed to them, more especially as in some other cases the actual values for menthyl esters have had to be modified from time to time to a very material extent.

The interesting rule, which Cohen has based on these and other results, *that the rotatory effect of the ortho-grouping differs more from that of the phenyl than do those of the meta- and para-groupings,* does not contradict my rule with regard to the order of the rotatory effects themselves; it is not only independent of, but also quite consistent with, it.

Another series of menthyl esters prepared by Cohen illustrates my rule in the reverse order in a particularly interesting manner:

Position Isomerism and Optical Activity (J. B. Cohen, Trans., 1911, **99**, 1059).

	$[\mathrm{M}]_{\mathrm{D}}^{20^{\circ}}$.	$[\mathrm{M}]_{\mathrm{D}}^{100^{\circ}}$.
Menthyl benzoate	−239°	−232·7°
,, *o*-iodobenzoate	237	236
,, *m*-iodobenzoate	237	233·5
,, *p*-iodobenzoate	237	224·0

In this series the differences for $[\mathrm{M}]_{\mathrm{D}}^{20^{\circ}}$ are altogether obliterated, but for $[\mathrm{M}]_{\mathrm{D}}^{100^{\circ}}$ we have the order of values:

ortho>meta>phenyl>para,

the difference between the values for meta and phenyl being so small that it cannot be regarded as of any significance.

The following series, which have been prepared in my laboratory, exhibit the effect of position-isomerism on optical activity in a particularly striking and instructive manner:

Position Isomerism and Rotatory Effect (P. Frankland and H. Aston, Trans., 1899, **75**, 493).

	$[\mathrm{M}]_{\mathrm{D}}^{20^{\circ}}$.	$[\mathrm{M}]_{\mathrm{D}}^{100^{\circ}}$.
Methyl dibenzoylglycerate	+87·5°	+57·2°
,, *o*-toluylglycerate	71·9	46·6
,, *m*-toluylglycerate.........	94·0	58·6
,, *p*-toluylglycerate	146·7	89·3
Ethyl dibenzoylglycerate	+89·2	+61·7
,, *o*-toluylglycerate	80·1	51·1
,, *m*-toluylglycerate..	99·5	64·4
,, *p*-toluylglycerate	156·9	96·9

Another series which illustrates my rule in the reverse order is the following:

Position Isomerism and Rotatory Effect (P. Frankland and F. M. Wharton, 1899, **75**, 337).

			$[\mathrm{M}]_{\mathrm{D}}^{136^{\circ}}$.
Methyl benzoylmalate	$[\mathrm{M}]_{\mathrm{D}}^{21^{\circ}}$	−15·0°	−36·3°
,, *o*-toluylmalate	$[\mathrm{M}]_{\mathrm{D}}^{23^{\circ}}$	25·0	39·5
,, *m*-toluylmalate	$[\mathrm{M}]_{\mathrm{D}}^{20^{\circ}}$	17·8	37·8
,, *p*-toluylmalate	$[\mathrm{M}]_{\mathrm{D}}^{18\cdot5^{\circ}}$	8·8	28·4
Ethyl benzoylmalate	$[\mathrm{M}]_{\mathrm{D}}^{21^{\circ}}$	11·4°	35·5°
,, *o*-toluylmalate	,,	19·3	37·0
,, *m*-toluylmalate............	,,	14·4	35·9
,, *p*-toluylmalate	$[\mathrm{M}]_{\mathrm{D}}^{20^{\circ}}$	0·7	22·5

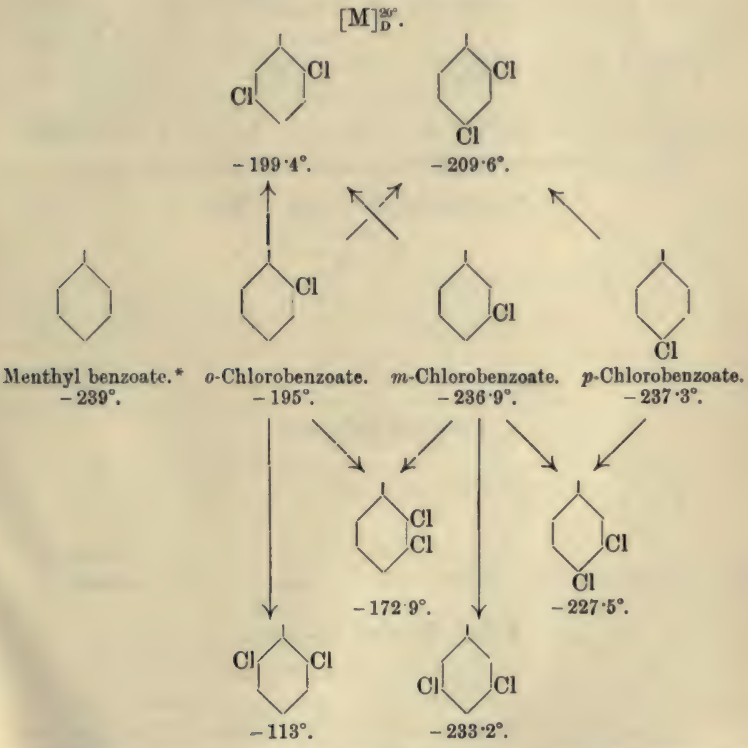
Thus it will be seen that approximately the reverse order of magnitudes holds good:

para<phenyl<meta<ortho.

The correlation of position isomerism with optical activity has been extended by the systematic investigations of Cohen and his pupils to the trisubstituted benzenes—more especially the dichlorobenzoic acid derivatives of menthol.

In this series the most striking feature is, again, the depressing influence of the diortho-position (2:6-dichlorobenzoic acid). The relative rotatory effects of the six different groupings are easily seen from the following table, to which have also been added the results of Pickard and Littlebury (Trans., 1907, **91**, 300) on some of the xylenyl derivatives of menthylcarbamic acid.

Menthyl Chloro- and Dichloro-benzoates (Cohen and Briggs, Trans., 1903, **83**, 1214).



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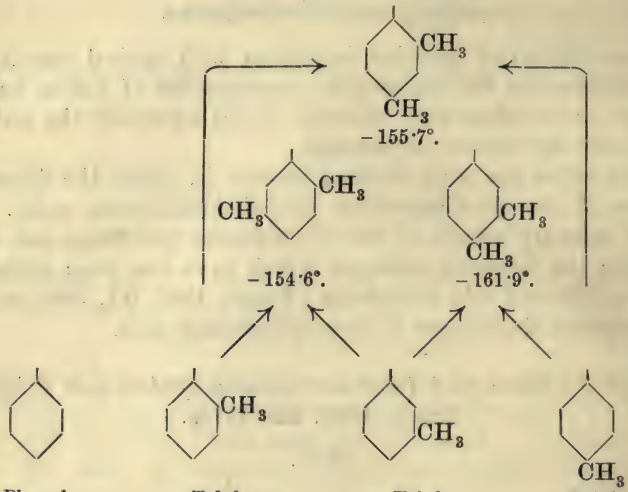
* Trans, 1910, **97**, 1734.

Menthylcarbamates (Pickard and Littlebury, Trans., 1907, **91**, 304).

Chloroform Solution. $[M]_D^{20^\circ}$.

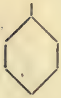


Phenyl.	*o*-Tolyl.	*m*-Tolyl.	*p*-Tolyl.
-159°.	-158·2°	-161·4°.	-162·6°.

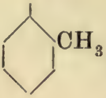
The following are further examples of *o*-, *m*-, and *p*-compounds:

Menthylcarbamides (Pickard and Littlebury, *loc. cit.*).

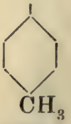
Chloroform Solution. $[M]_D^{20^\circ}$.



Phenyl.
-191°.

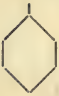


o-Tolyl.
-161·7°.

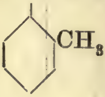


p-Tolyl.
-196·3°.

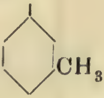
Pyridine Solution.



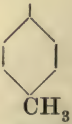
-223·1°.



-219·8°.

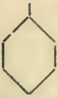


-235·1°.

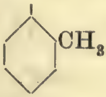


-233·7°.

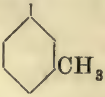
Ethyl Alcohol Solution.



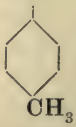
-214·6°.



-190°.



-217·5°.



-245·5°.

(6) *Comparative Rotatory Effect of Cyclic Groupings.*—The relative rotatory effect of different cyclic groupings has also been investigated; thus the furan ring has been compared with the benzene ring by determining the rotation of the pyromucyl-, benzoyl-, and toluyl-tartrates.

	$[\mathrm{M}]_{\mathrm{D}}^{100^\circ}$
* Ethyl dibenzoyltartrate †	-251.6°
,, di-*o*-toluyltartrate	241·9
,, di-*m*-toluyltartrate	281·7
,, di-*p*-toluyltartrate	397·7
‡ ,, dipyromucyltartrate	266·5

* Frankland and Wharton, Trans., 1896, **69**, 1583.

† The order of the magnitudes should be again noted:

ortho < phenyl < meta < para.

‡ Frankland and F. W. Aston, Trans., 1901, **79**, 514.

In all of these, of course, conjugated groupings occur, and the benzoic, toluic, and pyromucic acids are $\Delta^{\alpha\beta}$-acids; hence great exaltation of the rotation is to be expected according to Rupe and Hilditch, and actually occurs.

Again, by introducing various cyclic groups into tartramide, a more extended series of comparisons has been effected.

Tartaric Amides.

	$[\mathrm{M}]_{\mathrm{D}}^{20^\circ}$ in pyridine solution.		$[\mathrm{M}]_{\mathrm{D}}^{20^\circ}$ in pyridine solution.
Methylamide	$+279^\circ$	Furfurylidenehydrazide	$+736^\circ$
n-Heptylamide	305	Anilide	739
ac-Tetrahydro-β-naphthylamide	240	*o*-Toluidide	667
Benzylamide	300	*m*-Toluidide	730
Furfurylamide	307	*p*-Toluidide	793
α-Naphthylamide	400	*ar*-Tetrahydro-β-naphthylamide	840
Benzylidenehydrazide	554	β-Naphthylamide	1160

P. Frankland and Slator, Trans., 1903, **83**, 1349.
P. Frankland and Ormerod, *ibid.*, 1342.
P. Frankland and Twiss, *ibid.*, 1906, **89**, 1852.

Particularly noteworthy in this series are:

(*a*) The low rotatory effect of the *ac*-tetrahydro-β-naphthyl group.

(*b*) The close equivalence of the benzyl and furfuryl groups.

(*c*) The depressing influence on rotatory effect of the ortho-positions in the α-naphthyl and *o*-toluyl groups.

(*d*) The exalted rotatory effect of the para-position in the β-naphthyl and in the *ar*-tetrahydro-β-naphthyl groups.

The following menthyl compounds described by Rupe are also of interest in this connexion:

Nine per cent. Ethyl-alcoholic Solutions (Rupe).

	$[M]_D^{20^\circ}$.		$[M]_D^{20^\circ}$.
Menthyl *cyclo*propanecarboxylate...	−153·5°	butyrate.........	−164·7°
,, *cyclo*butanecarboxylate ...	164·4	valerate	165·7
,, *cyclo*pentanecarboxylate...	171·3	caproate.........	164·7
,, *cyclo*hexanecarboxylate ...	157·3	heptoate.........	166·0
,, benzoate	217·2		
,, Δ^1-*cyclo*hexenecarboxylate	197·0		
,, Δ^2-*cyclo*hexenecarboxylate	156·9		

These results show that the cyclic arrangement, especially if saturated, does not by any means necessarily involve an exaltation of the rotatory effect. On the other hand, if the asymmetric carbon atom itself forms part of a ring, an increase, and generally a very great increase, in the rotatory effect occurs.

Time does not permit me to make mention of many other investigations which have been carried out on the relationship between chemical constitution and the degree of optical activity, nor can I do more than barely refer to those heroic efforts which have been made by Patterson and his pupils to introduce some order into the bewildering phenomena of rotation in solution. In this, as in practically all other branches of the study of optical activity, investigators, in the absence of any comprehensive and guiding generalisation, are indeed carrying out one of Pasteur's favourite injunctions to his collaborators when in similar difficulties: "*Amassons des faits pour avoir des idées.*"

Walden Inversion.

There is perhaps no branch of stereochemistry to which more attention has recently been devoted than to those remarkable enantiomorphous transformations first discovered independently by Walden and by Tilden, Forster, and Marshall, and which have come to be known as "Walden Inversions." The particular interest attaching to these changes is the circumstance that they were not foreseen in the theoretical considerations concerning asymmetry by either Pasteur, Le Bel, or van't Hoff. The number of these transformations on record has now been greatly multiplied, more especially through the striking investigations of Emil Fischer, McKenzie, and their pupils.

In this field, again, although a large amount of experimental material has been accumulated with great labour and success, little or no progress has been made in furnishing any explanation based on experimental evidence.

Having vainly sought a cause for this remarkable transformation, the baffled investigators are now turning round and saying that the phenomenon is not remarkable at all, and that it is incidental to substitution in general. In substitution it is suggested that the group introduced does not necessarily take the place of the one substituted, but that a rearrangement or shuffle of the groups may occur, and that it depends on the mutual affinities of the several groups as to whether the entering group or a group already attached to the carbon atom takes the exact place formerly occupied by the group which has been removed; thus substitution at an asymmetric carbon atom may occur (*a*) *without change of configuration*, (*b*) *with production of the enantiomorphous configuration* (*inversion*), and (*c*) *with both of these processes occurring simultaneously* (*racemisation partial or complete*).

Substantially the same views on this important subject have been arrived at by Emil Fischer and by Werner quite independently, and from a consideration of entirely distinct experimental data in each case.

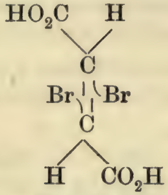
That there should be this concurrence of opinion is the less surprising since the views expressed are but little more than a statement of the principle that in substitution the entering group does not necessarily take the place of the group removed. The discovery of the Walden Inversion has made the concession of this principle inevitable, and although both Emil Fischer and Werner suggest a hypothetical mechanism whereby such a rearrangement can be accomplished, there does not appear at present to be any means by which the operation of this mechanism can be tested, nor has the assumption of the existence of this mechanism so far enabled any actual occurrence to be predicted.

The more immediate gain to chemical theory which has accrued from the discovery of the Walden Inversion is, therefore, that it has enabled us to obtain a deeper insight into the process of substitution, revealing as it does that this is not necessarily a process of mere replacement, but that a simultaneous rearrangement of the relative positions of the groups attached to the particular atom may unquestionably occur.

Fumaric and Maleic Acids.

Very closely related to the phenomenon of the Walden Inversion are the remarkable transformations of fumaric and maleic acids into disubstituted succinic acids, in which the racemic and meso-forms of the latter are produced in what would appear to be the most capricious and contradictory manner.

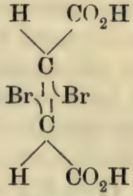
Our knowledge of these transformations has recently been very materially extended by the valuable work of McKenzie (Proc., 1911, **27**, 150) as well as of Holmberg (Abstr., 1912, i. 4), who have definitely proved that the dibromosuccinic acid obtained from fumaric acid is the meso-, and that from maleic acid the racemic form, this being just the opposite of what would be anticipated from a consideration of the space-formulæ of the acids in question. These transformations involve in each case what may be called the *cross-saturation* by bromine of the double bond in fumaric and maleic acids respectively; thus:



Fumaric acid.

↓

Dibromosuccinic acid (meso-).



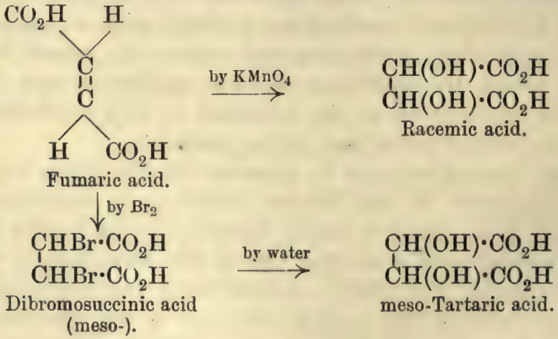
Maleic acid.

↓

*iso*Dibromosuccinic acid (racemic).

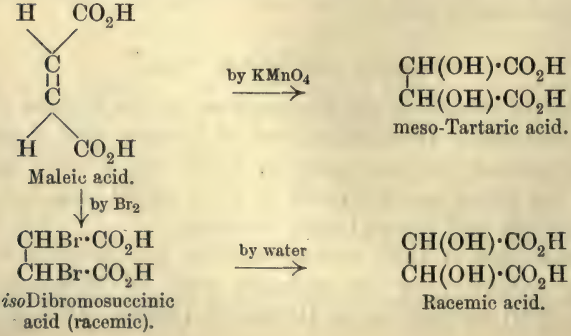
whilst if the two bromine atoms were to break only one of the two bonds of the ethylenic linking, then fumaric would lead to the racemic, and maleic to the meso-dibromosuccinic acid.

Thus on reviewing the well known transformations, we have:



Fumaric acid. Racemic acid.

Dibromosuccinic acid (meso-). meso-Tartaric acid.



Maleic acid. meso-Tartaric acid.

*iso*Dibromosuccinic acid (racemic). Racemic acid.

The steric significance of these transformations being now placed beyond doubt, it would appear to be a fitting opportunity for reconsidering the material pictures with which we have come to visualise these and other changes.

It is now well recognised that the bold and most ingenious adaptation by Wislicenus of the van't Hoff models to the explanation of the changes suffered by ethylenic and acetylenic compounds, although highly stimulating and suggestive at the time, is quite out of harmony with many of the known facts. Indeed, the Wislicenus theory may be said to have fully justified itself from one point of view by having provoked that weighty and merciless indictment by Michael, which is certainly amongst the classics of chemical literature.

As is well known, the criticism of Michael, Lossen, and others led to the proposal of a new scheme by Pfeiffer,* in which an attempt was made to bring these bewildering metamorphoses into line with the symbolism used by Werner for the phenomena of inorganic chemistry. In Pfeiffer's formulation, however, the conceptions of van't Hoff with regard to directed valency, which have proved so fertile in connexion with the saturated carbon compounds, are practically discarded. To most chemists this must surely appear like throwing away a pearl of priceless worth, and it therefore behoves those who value the classical imagery of van't Hoff to make every endeavour to use it, if at all possible, for the explanation of the properties of carbon compounds in general.

I would therefore venture to bring forward some ideas which have occurred to me in connexion with the application of the van't Hoff formulæ to the ethylenic and acetylenic compounds and their transformations.

In considering the possibilities of addition to unsaturated molecules, the striking phenomena which have been attributed to steric hindrance force themselves on our attention. The phenomena of steric hindrance are, moreover, particularly pronounced in the case of *αβ*-unsaturated acids, as has been recently shown by Thomas and Sudborough in a very important paper on the esterification of saturated and unsaturated acids (this vol., p. 320) respectively. *Thus when two extraneous atoms or groups become united to a pair of unsaturated carbon atoms, it appears to me only reasonable to suppose that there would be difficulty, from spatial limitations, to their becoming both attached on the same side of the pair of carbon atoms; and that there will, in consequence, be a tendency for them to attach themselves on opposite sides of the pair of acetylenic or*

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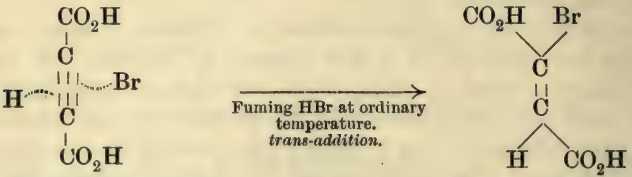
* "Beitrag zur Stereochemie d. Kohlenstoffverbindungen speziell der ungesättigten Systeme," Pfeiffer (*Zeitsch. physikal. Chem.*, 1904, **48**, 40).

ethylenic carbon atoms, leaving the latter in either the ethylenic or saturated state of union respectively.

Thus what may be *trans-addition* of Br_2, of HBr, of HCl, etc., to acetylenedicarboxylic acid, or to fumaric or maleic acids, which was inadmissible under the Wislicenus interpretation of the triple and double bonds, becomes the most natural and probable mode of attachment if the limitations of space, on the one hand, and the more modern and less constrained conceptions of the acetylenic and ethylenic unions on the other, be taken into account.

A few concrete examples will illustrate the application of this principle of trans-addition most clearly:

Bandrowski (*Ber.*, 1882, **15**, 2694).



Acetylenedicarboxylic acid. Bromofumaric acid.

This transformation must depend on direct trans-addition of HBr, and not to preliminary formation of bromomaleic acid, because Michael has shown (*J. pr. Chem.*, 1892, [ii], **46**, 222) that the latter remains unchanged in the presence of hydrobromic acid.

Similarly, fuming hydrochloric and hydriodic acids yield chloro- and iodo-fumaric acids respectively.

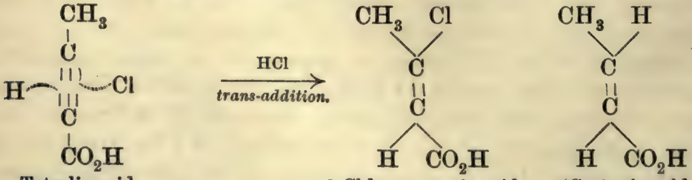
Again, Michael (*J. pr. Chem.*, 1892, [ii], **46**, 221) has shown that by addition of Br_2 to acetylenedicarboxylic acid there are formed:

Dibromofumaric acid	70 per cent.
Dibromomaleic acid	30 per cent.

and the ester also gave almost the same proportion of the two products.

Of similar reactions may be mentioned:

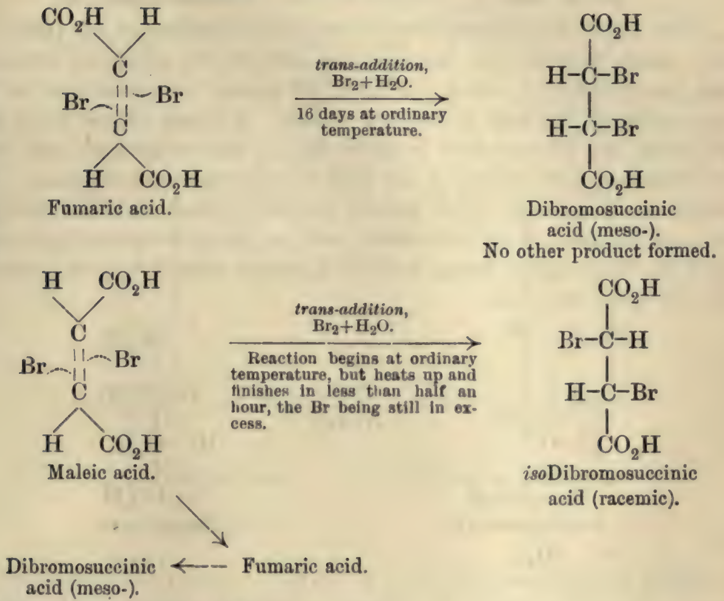
Friedrich (*Annalen*, 1883, **219**, 370).



Tetrolic acid. β-Chlorocrotonic acid (fumaroid). Crotonic acid.

Reduction. *trans-addition* of H_2.

Petri (*Annalen*, 1879, **195**, 56).


Fumaric acid.
trans-addition, Br₂+H₂O.
16 days at ordinary temperature.
Dibromosuccinic acid (meso-).
No other product formed.
Maleic acid.
trans-addition, Br₂+H₂O.
Reaction begins at ordinary temperature, but heats up and finishes in less than half an hour, the Br being still in excess.
isoDibromosuccinic acid (racemic).
Dibromosuccinic acid (meso-).
Fumaric acid.

This is formed when the mixture is allowed to remain until the bromine has disappeared, and its formation is obviously due to the action of bromine on the fumaric acid first formed.

This simultaneous production of fumaric acid * is probably due to catalytic conversion of maleic acid, similar to that which takes place when maleic acid is heated by itself. The various transformations observed by Skraup are also to be interpreted as catalytic changes, the mechanism of which I do not propose to discuss.

Michael (*J. pr. Chem.*, 1895, [ii], **52**, 352), in his exhaustive digest of the ascertained facts bearing on this subject, states that he knows of no single exception to the rule that, *by the addition of halogen acid to an αβ-acetylenic acid, αβ-halogen ethylenic acid of fumaroid form (higher m. p.) is produced.* In other words, all these cases conform to what I would call the *Principle of Trans-addition.*

An apparent exception to this principle of trans-addition will, however, have doubtless occurred to you; for, as we have already seen:

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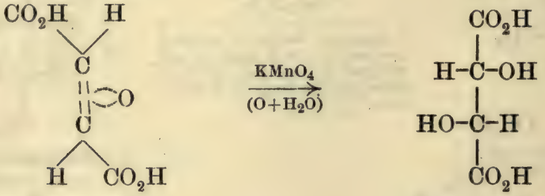
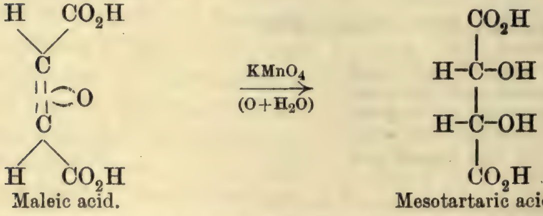
* McKenzie finds that the production of fumaric acid is greatly diminished if the bromine is used in anhydrous ether (Proc., 1911, **27**, 150).

$$\left.\begin{array}{l}\text{Fumaric acid}\\ \\ \text{Maleic acid}\end{array}\right\} \xrightarrow[\text{addition of (HO)}_2]{\text{Oxidation with KMnO}_4} \left\{\begin{array}{l}\text{Racemic acid}\\ \\ \text{Mesotartaric acid}\end{array}\right.$$

Now these transformations involve *cis*-attachment of $(HO)_2$ in each case, that is, the development out of the ethylenic union of the two bonds, by which the two OH-groups are attached, on the same side of the pair of carbon atoms. We can escape from this difficulty, as Werner and Pfeiffer do, by assuming that one atom of oxygen is first added to the pair of ethylenic carbon atoms. *The addition of a single atom would naturally take place on one side only of the pair of carbon atoms, and, on the subsequent hydroxylation of this oxygen atom, both OH-groups would remain attached on the same side*, thus:



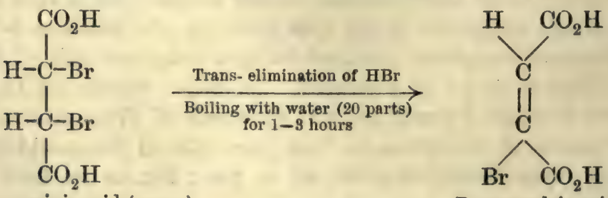
Fumaric acid. Racemic acid.



Maleic acid. Mesotartaric acid.

Thus the conceptions of van't Hoff, if freely interpreted, appear to be quite capable of adaptation to the phenomena of addition exhibited by unsaturated carbon compounds. We will now consider some of those numerous reactions in which two univalent atoms or groups are eliminated from the molecule.

Fittig and Petri (*Annalen*, 1879, **195**, 56).


CO2H
H-C-Br
H-C-Br
CO2H
Trans- elimination of HBr
Boiling with water (20 parts) for 1—3 hours
H
CO2H
C
C
Br
CO2H

Dibromosuccinic acid (meso-). Bromomaleic acid.*

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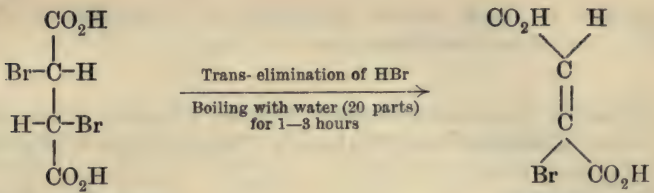
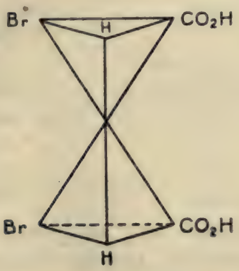
* Michael (*J. pr. Chem.*, 1895, [ii], **52**, 304) found that potassium hydrogen bromomaleate is converted, in solution at the ordinary temperature, into bromo-

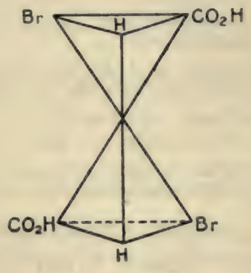

Trans- elimination of HBr
Boiling with water (20 parts) for 1—3 hours

*iso*Dibromosuccinic acid (racemic).

Bromofumaric acid.



Dibromosuccinic acid
(meso-).
(Stronger acid.)



*iso*Dibromosuccinic acid
(racemic).
(Weaker acid.)

The trans-elimination of HBr in these dibromosuccinic acids requires explanation. It is necessary that the groups should be orientated in the most stable position as the result of the rotation of the carbon atoms on the single bond uniting them. Judging by analogy from the fact that maleic acid is a stronger acid than fumaric acid, it may be concluded that the stronger meso-dibromosuccinic acid has the carboxyl groups turned towards each other, whilst the weaker *iso*dibromosuccinic acid should have the carboxyl groups averted from each other. It is in these positions that the trans-elimination of HBr is necessitated to obtain the above products. *If the groups are so orientated, cis-elimination of* HBr *is impossible.*

The *cis-* or *trans*-interpretation of the removal of two atoms from a saturated dibasic acid must obviously depend on the manner in which the groups attached to the two carbon atoms which will enter into ethylenic union in the process are orientated. I have just indicated that light may be thrown on the orientation of the two carboxyl groups in two such isomeric acids by a consideration of their relative strength, inasmuch as the stronger of the two may reasonably be supposed to have these groups approximated, whilst in the weaker of the two these groups will be averted from each other. In the following table I have given the available data

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fumarate, and explains the fact that, in the above hydrolysis of dibromosuccinic acid with water, 2—3 per cent. of bromofumaric acid are actually obtained.

indicative of these relative strengths for a number of the acids bearing on these considerations:

Dissociation Constants (Ostwald, *Zeitsch. physikal. Chem.*, 1889, **3**, 170; Kohlrausch and Holborn's "Leitvermögen d. Elektrolyte," 1898, p. 176).

	K.
Fumaric acid	0·09
Maleic acid	1·2
Mesotartaric acid	0·060
Racemic acid	0·097
Crotonic acid (Me and CO_2H *trans.*), m. p. 72°	0·0020
*iso*Crotonic acid (Me and CO_2H *cis*), m. p. 34°	0·0036
α-Chlorocrotonic acid, m. p. 99°	0·072
α-Chloro*iso*crotonic acid, m. p. 66°	0·158
β-Chlorocrotonic acid, m. p. 94°	0·0144
β-Chloro*iso*crotonic acid, m. p. 61°	0·0095*

The dissociation constants of dibromo- and *iso*dibromo-succinic acids do not appear to have been determined, but the former acid is evidently the stronger from a consideration of their conductivities:

	$\frac{\text{Litre}}{\text{gram mol.}} = \phi_1$.	$v_1 = 10^{-3}\phi_1$ λ for v_1.	$2v_1$.	$4v_1$.	$8v_1$.	$16v_1$.	$32v_1$.
Dibromosuccinic acid	138·5	393	460	531	595		
*iso*Dibromosuccinic acid	65·2	302	349	394	441	494	547

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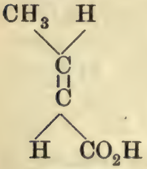
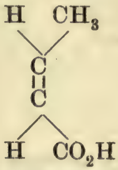
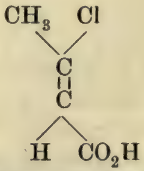
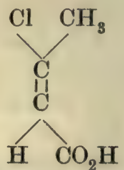
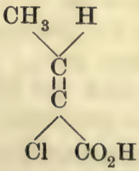
* Inspection of the configuration of the β-chlorocrotonic acids shows that the *iso*-acid should be the weaker of the two, notwithstanding that *iso*crotonic acid is stronger than crotonic acid, thus:

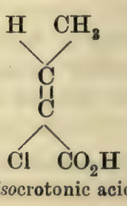

Crotonic acid (weaker).


*iso*Crotonic acid (stronger).


β-Chlorocrotonic acid (stronger because of approximation of Cl and CO_2H).


β-Chloro*iso*crotonic acid (weaker because of aversion of Cl and CO_2H).


α-Chlorocrotonic acid (weaker).


α-Chloro*iso*crotonic acid (stronger.)

Dissociation Constants (continued).

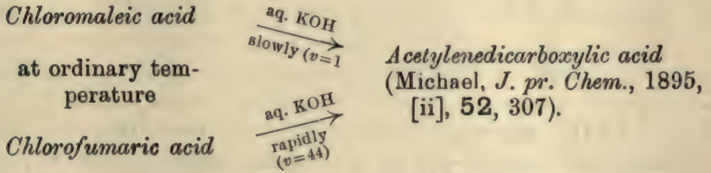
	K.		K.
Mesaconic acid (*trans*)	0·079	α-Bromocinnamic acid	1·44
Citraconic acid (*cis*)	0·34	β-Bromocinnamic acid	0·093
Tiglic acid	0·001	*m*-Phthalic acid	0·029
Angelic acid	0·0050	*o*-Phthalic acid	0·121
Tetrolic acid	0·246	Malic acid	0·0395
Phenylpropiolic acid	0·59	Succinic acid	0·0066
Cinnamic acid (*trans*)	0·0035	Monochlorosuccinic acid	0·28
*iso*Cinnamic acid (*cis*)	0·0156	Monobromosuccinic acid	0·28

Very significant as regards the possibility of trans-elimination is the fact observed by Michael (*J. pr. Chem.*, 1892, [ii], **46**, 230) that:

$$\textit{Dibromofumaric ester} \xrightarrow[\text{moist ether at } 68^\circ]{\text{reduced by Zn in}} \textit{Acetylenedicarboxylic ester}$$

especially as this is not a violent reaction, and *must involve trans-elimination.* Dibromomaleic ester is less easily reduced.

Other similar facts may be added, thus:

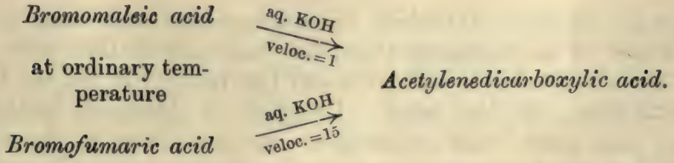


(Michael, *J. pr. Chem.*, 1895, [ii], **52**, 307).

At 100° the two velocities become almost identical.

Michael suggests that the proximity of the two carboxyls to the chlorine atom in chlorofumaric acid loosens the attachment of that atom to the carbon, and therefore predisposes it to elimination.

Similarly,

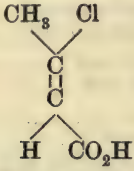


According to Michael, this is a general rule that the fumaroid loses halogen acid more readily than the maleinoid form. In other words, *trans-elimination is the rule.*

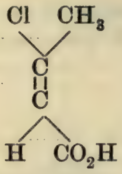
Again, the following instances may be cited as examples of the greater facility with which trans- as compared with cis-elimination of halogen acid takes place:

trans-Elimination of Halogen Acid. (Easy.)

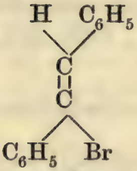
cis-Elimination of Halogen Acid. (Difficult.)



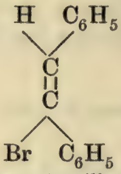
β-Chlorocrotonic acid,* m. p. 94°.



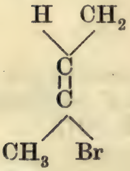
β-Chloro*iso*crotonic acid, m. p. 61°.



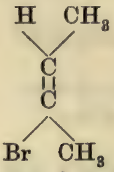
Bromostilbene,† m. p. 31°.



Bromo*iso*stilbene, m. p. 19°.



Bromobutylene,‡ b. p. 87—88°. (Obtained from angelic acid.)



Bromobutylene, b. p. 93—94°. (Obtained from tiglic acid.)

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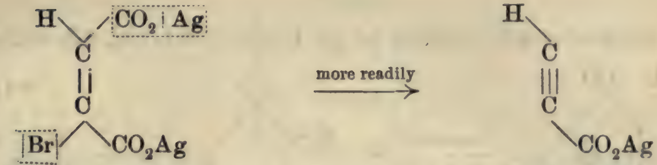
* Michael, *J. pr. Chem.*, 1892, **46**, 255

† Wislicenus and Seeler, *Ber.*, 1895, **28**, 2693. Otto and Stoffel, *Ber.*, 1897, **30**, 1799.

‡ Liebermann, *Annalen*, 1900, **313**, 216, 231, 249.

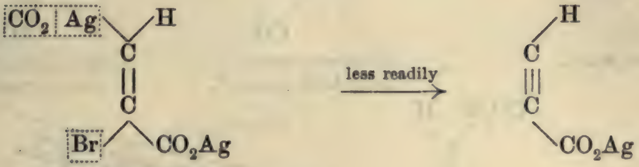
In these reactions, therefore, trans-elimination *must* take place in the case of the fumaroid form, but inasmuch as the maleinoid form also loses halogen acid, although less readily, it follows that cis-elimination *can* also occur. Moreover, if Michael's explanation of the more ready elimination by the fumaroid form be accepted, it is not necessary to regard trans-elimination as, *per se*, the more favoured process.

On the other hand, the silver salts of bromomaleic and bromofumaric acids lose carbon dioxide and silver bromide in aqueous solution at 100°, and the maleinoid loses these more readily than the fumaroid form. *The loss in the case of the maleinoid must be by trans-elimination, whilst in that of the fumaroid form it must be by cis-elimination*:



Silver bromomaleate.

Silver propiolate.



Silver bromofumarate.

These reactions are generally cited as showing that trans- takes place more readily than cis-elimination, but as a matter of fact it has been shown by Kekulé and by Scherks (see footnote) that when the silver salts themselves are boiled with water it is the bromofumarate, and not the bromomaleate, which readily decomposes. This is, moreover, what would be anticipated, since the bromine atom should be more reactive in the fumarate owing to its proximity to two carboxyl groups. It would appear, therefore, that in this case cis-elimination is the more favoured process under the conditions prevailing in the experiments of Kekulé and Scherks.

Similar relations are found to exist for bromocitraconic (mal.) and bromomesaconic (fum.) acids. (Both these and the above are the observations of Michael,* see footnote).

We will now consider some further remarkable reactions of maleic and fumaric acids; thus both dibromosuccinic and *iso*dibromosuccinic esters yield fumaric ester on reduction with zinc and moist ether:

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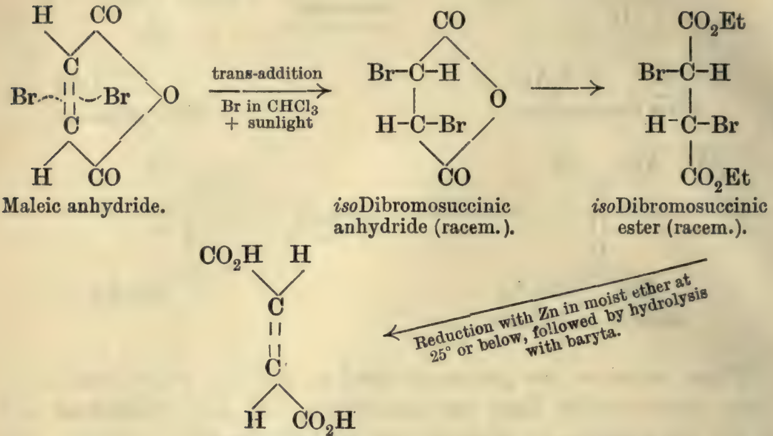
* Michael (*J. pr. Chem.*, 1895, [ii], **52**, 313) uses the free acids with calculated quantities of silver nitrate; the silver salts thus remain in the presence of the free nitric acid formed by the interaction.

Kekulé found (*Annalen*, 1864, **130**, 8) that silver bromofumarate, in nitric acid solution, gave no silver bromide on boiling, but he observed that the silver salt itself was easily decomposed on boiling with water (*loc. cit.*, p. 10), whilst silver bromomaleate was not easily decomposed on boiling with water. Scherks (*Annalen*, 1885, **227**, 235) similarly noticed that boiling silver maleate with water hardly led to any decomposition even after days.

Owing to the different results obtained, apparently according to the different conditions employed, these reactions do not at present lend themselves to being used in this discussion as to the relative facility with which cis- and trans-elimination take place.

Michael and Schulthess (*J. pr. Chem.*, 1891, [ii], **43**, 592).



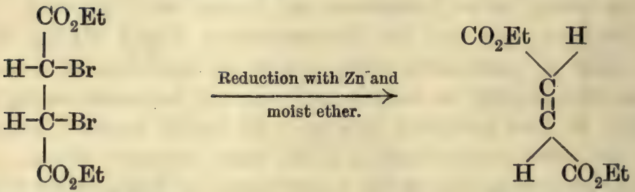
Maleic anhydride.

*iso*Dibromosuccinic anhydride (racem.).

*iso*Dibromosuccinic ester (racem.).

Fumaric acid.

trans-addition
Br in $CHCl_3$ + sunlight
Reduction with Zn in moist ether at 25° or below, followed by hydrolysis with baryta.

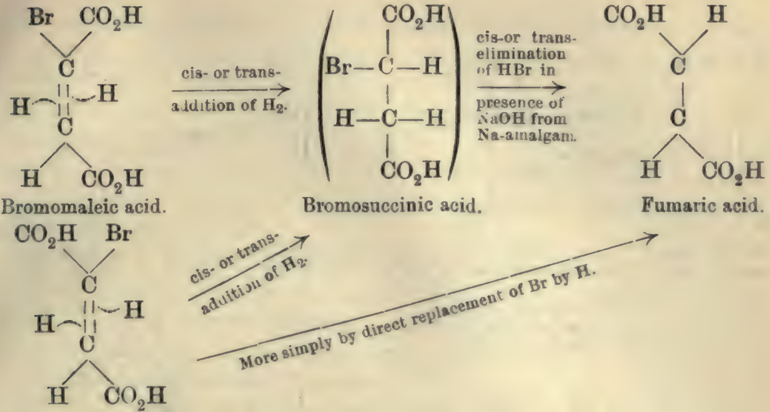


Dibromosuccinic acid (meso-).

Fumaric ester.

The simplest explanation of the fact that both dibromosuccinic and *iso*dibromosuccinic esters yield fumaric ester on reduction is that in both cases, by replacement of one atom of bromine by hydrogen, one and the same monobromosuccinic ester is formed, and that this *by either cis- or trans-elimination* of hydrogen bromide by the zinc can only yield a fumaric derivative *provided that the orientation of the groups in monobromosuccinic acid is such that the carboxyls are averted from each other.* If the carboxyl groups were directed towards each other, then maleic ester would result from either cis- or trans-elimination, assuming no rotation to occur after the elimination.

This would also account for the fact observed by Petri (*Annalen*, 1879, **195**, 65) that the sodium salts of both bromomaleic and bromofumaric acids, on reduction with the calculated amount of sodium amalgam, yield fumaric acid only, thus:



Bromomaleic acid. Bromosuccinic acid. Fumaric acid.

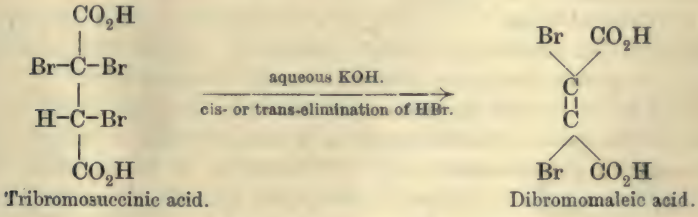
Bromofumaric acid.

The cis- or trans-elimination can only give rise to fumaric acid if in the hypothetically formed bromosuccinic acid the carboxyl groups are averted from each other.

In both cases some succinic acid is also formed, but no maleic acid.

An acid obviously corresponding with monobromosuccinic acid is tribromosuccinic acid, which with aqueous alkali gives dibromomaleic acid in a practically pure state (Michael, *J. pr. Chem.*, 1892, [ii], **46**, 223).

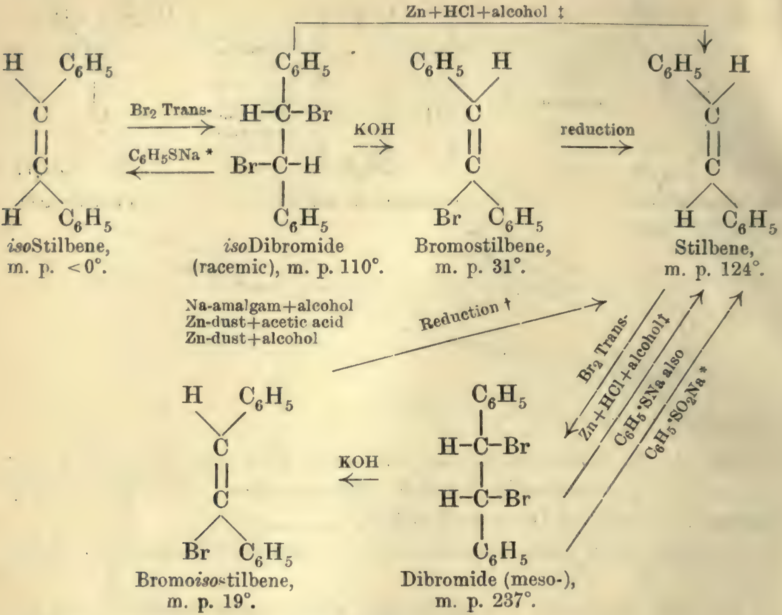
This necessitates the two carboxyl groups being directed towards each other (unlike in monobromosuccinic acid), and the HBr-elimination may be either cis or trans:



Tribromosuccinic acid. Dibromomaleic acid.

Stilbene and iso*Stilbene Compounds.*

The transformations which these undergo are very instructive from the point of view of addition and elimination, presenting as they do a complete analogy to the fumaric and maleic changes already discussed; thus:



* Otto and Stoffel (*Ber.*, 1897, **30**, 1799).

† Limpricht and Schwanert (*Annalen*, 1870, **155**, 72); Aronstein and Holleman (*Ber.*, 1888, **21**, 2831).

‡ Otto and Stoffel (*Ber.*, 1897, **30**, 1800) used Zn + HCl + alcohol They found that the *iso*dibromide was much more slowly reduced than the dibromide.

The consideration of the various phenomena to which I have referred leads me to suggest:

(1) That addition to an acetylenic or ethylenic union takes place preferentially, sometimes almost exclusively, by the two univalent atoms or groups becoming attached in the *trans*-position.

(2) That a notable exception to this rule is to be found in the case of the oxidation of fumaric and maleic acids to racemic and mesotartaric acids respectively. If, however, it be supposed that in this case an oxide is first formed, and that this is subsequently hydroxylated, then the departure from the above rule is only apparent, but not real.

(3) Having regard to the phenomena of steric hindrance, the attachment of two univalent atoms or groups on opposite sides of an ethylenic or acetylenic union, that is, in the *trans*-position, would appear to be the most natural and favoured. The phenomena of steric hindrance have, moreover, been found to be especially pronounced in the case of $\alpha\beta$-unsaturated acids.

(4) That the elimination of two univalent atoms or groups from their union with two adjacent carbon atoms can, in all cases investi-

gated, be accounted for by preferential extrusion of the two atoms or groups in the *trans*-position, but that in some cases the formulæ admit of either cis- or trans-extrusion with the same result.

(5) That in some cases the elimination *must* take place in the *trans*-position, and that in a great number of cases, in which the facility of elimination can be compared in maleinoid and fumaroid isomerides, the trans-elimination takes place more readily than the cis-elimination.

(6) That in all the cases which I have considered this preferential trans-elimination can be accounted for with some degree of plausibility as being due to chemical forces (relative strength of acid, relative reactivity of halogen, etc.) predisposing to the trans- as contrasted with the cis-elimination.

(7) That, nevertheless, the uniformity with which trans-addition and trans-elimination appear to be the more favoured processes suggests that some common cause is at the root of both.

(8) That whilst the cause of preferential trans-addition may reasonably be supposed to depend on space limitations tending to interfere with cis-addition, it is more difficult, but by no means impossible, to suppose that a similar spatial limitation may favour the process of trans-extrusion. On the other hand, it is quite possible that the predisposition to trans-addition and trans-elimination may depend on an inherent tendency to centric symmetry in the development and in the abolition of pairs of valencies belonging to two carbon atoms which are united together. Such a tendency is, I take it, tacitly implied in the Pfeiffer scheme for these transformations.

In conclusion, I should like to add that our present greatly extended knowledge of these transformation phenomena connected with ethylenic and acetylenic compounds is primarily due to the genius and courage of Wislicenus in applying the van't Hoff conceptions to the elucidation of the previously inscrutable and apparently capricious behaviour of these unsaturated substances. It was the appearance of his classical memoir, "Ueber die Räumliche Anordnung der Atome in Organischen Molekülen und ihre Bestimmung in Geometrisch-Isomeren Ungesättigten Verbindungen," just a quarter of a century ago that provided the stimulus for those searching and critical investigations which were undertaken by Michael, Lossen, Fittig, and others in some of the most productive laboratories of the Old and New Worlds, and which have so largely added to the amount and to the accuracy of our knowledge bearing on this fascinating but difficult problem.

OBITUARY NOTICES.

JOHN ATTFIELD.

BORN AUGUST, 1835; DIED MARCH 18TH, 1911.

JOHN ATTFIELD was born in August, 1835, near Barnet, in Hertfordshire, the son of John Attfield, surveyor, of Whetstone. The name—originally At-the-fields, and later Atte Felde or Atefeld—is purely English, and it is therefore easy to trace the descent of John Attfield from the John Atefeld who flourished in "the Ville of Staundon" (now Standon, eight miles north-east of Hertford) as far back as 1361.

Attfield was educated at the school of the Rev. Alexander Stuart, then of Barnet, where he developed a taste for scientific pursuits as a direct result of the teaching he received. Having expressed a desire to be allowed to continue his studies in chemistry and physics, he was apprenticed, at the age of fourteen, for five years to Mr. William Frederick Smith, a pharmacist, of Walworth. During the last year of his apprenticeship, 1854, he attended the School of Pharmacy of the Pharmaceutical Society in Bloomsbury Square, and obtained the first prizes or medals in all subjects—namely, chemistry, pharmacy, materia medica, and botany. He passed the Minor or qualifying examination of the Society in the same year, and offered himself as a candidate for the Major examination, but was refused admission, as he was not of age. In September, 1854, he obtained the position of junior assistant to Dr. Stenhouse, F.R.S., lecturer on chemistry in the medical school at St. Bartholomew's Hospital, and subsequently became demonstrator of chemistry at the same hospital. Stenhouse was succeeded by Dr. (afterwards Sir Edward) Frankland, and Attfield remained with the latter as demonstrator, assisting him in research work, besides lecturing at the Addiscombe Military College, until 1862, when he was appointed director of the laboratories of the School of Pharmacy of the Pharmaceutical Society, and afterwards Professor of Practical Chemistry, which subject was given up by Prof. Redwood so that he might devote all his attention to the teaching of theoretical chemistry and pharmacy.

Shortly after his appointment Attfield went to Tübingen, where he obtained the degree of Doctor of Philosophy, presenting as his thesis a paper on "The Spectrum of Carbon," read before the Royal Society in June, 1862. Attfield remained Professor of Practical Chemistry at Bloomsbury Square until his retirement from public life in 1896.

He was elected a Fellow of the Chemical Society in 1862, and was a member of Council during the period 1874–8; was a Fellow, one of the founders of, and for several years a member of Council of the Institute of Chemistry; was elected a Fellow of the Royal Society in 1880; was an honorary member of the Pharmaceutical Society of Great Britain, and of some twenty other pharmaceutical colleges and societies all over the world.

Attfield was no less active in private than in public life; he took a keen interest in educational, philanthropic, social, and recreative movements in general, and was one of the leading spirits in the Herts Natural History Society and in the Watford Fieldpath Association. He retired practically from all public work in 1896; and, although suffering under rather severe physical disabilities, he was able to enjoy life in a very quiet way, his garden and his books being specially a great solace to him. He died at Ashlands, Watford, on Saturday, March 18th, 1911.

Attfield's published work deals almost exclusively with scientific pharmacy. During the time he was at St. Bartholomew's Hospital he wrote most of the chemical articles in "Brand's Dictionary of Art, Science, and Literature," and in the Arts and Science Division of the "English Cyclopædia," and he also found time to revise and extend the chemical portion of the fourth edition of Clegg's work on "The Manufacture and Distribution of Coal Gas." His first original paper, "On the Solubility of Mercurial Precipitates in Alkaline Salts," was read in November, 1859, to the Chemical Discussion Association of the Pharmaceutical Society, and was published in the *Chemical News* for 1860. From that time until 1897, he contributed between seventy and eighty papers to pharmaceutical and scientific literature.

In 1867 appeared the first edition of Attfield's "Manual of Chemistry: General, Medical, and Pharmaceutical," the basis of the work being some manuscript notes which the author had prepared for the students at St. Bartholomew's Hospital. The book has now reached its nineteenth edition.

Undoubtedly the greatest work of Attfield was in connexion with the "British Pharmacopœia." It is interesting to note that the name Johannes Attfield appeared in the prefatory pages of the "Pharmacopœia" of 1677, and of the reprints of 1678 and 1682, as one of the Fellows of the College of Physicians responsible for the production of the volumes, and he appears to have belonged to one and the same family as the editor of the 1898 "Pharmacopœia." On the appearance of the 1864 edition of the "Pharmacopœia," lectures were given at Bloomsbury Square by Profs. Bentley, Redwood, and Attfield, which with other criticisms aided in the suppression of the book and the appointment by the General Medical Council of Prof. Redwood and Mr. Warrington to edit a new edition. Redwood was also asked to edit the 1885 edition, but declined, and Attfield and Bentley became associated with him, and on the completion of the work Attfield was appointed Reporter in Pharmacy to the Pharmacopœia Committee and Editor of an Addendum to the "Pharmacopœia." In carrying out this work Attfield succeeded in bringing about the recognised co-operation of the General Medical Council and the Pharmaceutical Society and the imperialisation of the "Pharmacopœia," as evidenced by the publication, under his exclusive editorship, of the 1898 edition and the Indian and Colonial Addendum, his success being largely due to the nine Annual Reports (1886–94), "On the Progress of Pharmacy in Relation to the 1885 British Pharmacopœia," prepared by him for the General Medical Council. The reports, which aptly illustrate Attfield's method and thoroughness, show how much the medical profession was indebted to pharmacists for their voluntary efforts to make the "Pharmacopœia" a better book. Attfield received the thanks of the General Medical Council "for all that he had done to make the 'Pharmacopœia' complete and accurate."

One of the principal projects in which Attfield was interested, and of which he was one of the founders, was the British Pharmaceutical Conference, which has for its object the promotion of pharmaceutical research and of good fellowship among its members. The annual meetings of the Conference, inaugurated at Newcastle in 1863, have always been very successful, owing largely to Attfield's influence, in appreciation of which the members presented him with 500 volumes of general literature in 1880 on his retirement from official connexion with the Conference as its Honorary Secretary. In addition, this Association has ever since its foundation published a "Year-Book of Pharmacy," containing not only a full report of its meetings, but a digest of the scientific work bearing on Pharmacy published in other countries. The editorship of this publication was entrusted to Attfield, and retained by him for many years.

Attfield's views on education were always of the broadest type. He had a high opinion of the value of chemistry as a means of culture, considering that it taught the student—to quote his own words—"to observe accurately, reflect accurately, and describe accurately on all and any matters in general life."

He was a strong advocate of a curriculum of study, regarding the acquisition of knowledge merely for examination purposes as pernicious; hence he questioned any method of examining candidates which did not take note of the quality of the educational course which had been gone through. As a teacher he was pre-eminently kind and sympathetic, and the esteem in which he was held by his students may be gauged from the following extract from an address presented to Attfield in July, 1897, together with a silver tray and silver tea and coffee service, by his old pupils and friends:

"During the whole of this long tenure of his important office Prof. Attfield not only won and retained the respect of successive generations of students by the lucidity, accuracy, and thoroughness of his teaching, but he also endeared himself to them by his unfailing tact, kindness, and urbanity. Not less successfully did he serve pharmacists and medical practitioners, and through them the public, by his versatile ability, untiring energy, and power of organisation as an editor of the 'Pharmacopœia,' and author of a manual of chemistry, and generally as a worker who unceasingly applied the resources of the great science of chemistry to the demands of the great art of healing."

A. C.

JOHN MUTER.

BORN 1841; DIED DECEMBER 19TH, 1911.

JOHN MUTER was born in 1841 in Glasgow, where his father was Professor of Materia Medica. He studied chemistry at the Andersonian University under, and was for a time assistant to, Penny. His work was for some years mainly connected with the tuition of pharmacy at the "South London School of Pharmacy," founded by him, while, from the passing of the Food and Drugs Act in 1875 which created the systematic examination of food, he took an active interest in the development of food analysis. He was one of the founders of the Society of Public Analysts, and was from 1876 to 1891 one of the editors of *The Analyst*, to which journal he was a copious contributor on pharmaceutical and analytical subjects. Among his papers are notes on Cinchona bark, *spiritus aetheris nitrosi*, asafœtida and copaiba balsam, on the analysis of carbolic powders, condensed milk, butter, and methods for the estimation of glycerol and oleine. He was the author of a "Manual on Analytical Chemistry" and "An Introduction to Pharmaceutical and Medical Chemistry," both of which ran through a number of editions.

From 1879 to 1880 he was President of the Society of Public Analysts, and from 1896 to 1898 on the Council of the Institute of Chemistry. At one time or another he was Public Analyst for Bermondsey, Lambeth, Newington, Rotherhithe, Southwark, Wandsworth, part of Lincolnshire, and Analyst to the Metropolitan Asylums Board. At the same time he conducted an extensive private practice. He died on December 19th, 1911.

WALTHÈRE VICTOR SPRING.

BORN MARCH 6TH, 1848; DIED JULY 17TH, 1911.

ON March 1st, 1877, in the chemical lecture-room of the University of Liége, a large audience of students listened to a young man of twenty-nine, with the clearness of whose exposition and the originality of whose ideas everyone was struck; it was Walthère Spring, who was giving his inaugural lecture on general chemistry, and whose lectures were to be continued without interruption for thirty-four years.

He was born at Liége; his father, Frédéric Antoine Spring, was a Bavarian by birth, and had acquired Belgian citizenship through his eminent services as Professor of Anatomy and Physiology at the University of Liége. In the year 1839, when young Belgium was still struggling for the establishment of a good staff of professors in its universities—practically non-existent ten years before—the Minister of Public Instruction was so fortunate as to secure the collaboration of Frédéric Spring, then only twenty-five years of age; he attained great fame for the valuable and varied researches in histology, physiology, and botany he was able to carry out, notwithstanding his absorbing occupations of teacher and practising surgeon.

Walthère Spring inherited the brilliant qualities of his father, his facility and clearness of elocution, and his marvellous experimental skill; but living matter did not appeal to him particularly as a field of research, and, more or less against his father's will, he succumbed to the attraction that the inorganic world exercised for him.

In the year 1866 Spring entered the University of Liége, and gained the degrees of "Ingénieur des mines" and "Ingénieur des arts et manufactures." He then went to Bonn, where he attended Clausius's lectures on physics, and worked in the chemical laboratory of Kekulé, whose fame, together with his intimate relations with the Belgian scientific world during the time he held his professorship in Ghent, attracted Spring.

One is struck by the diversity as well as by the originality of the papers Spring presented to the Belgian Academy during the following four or five years: numerous studies on sulphur and its compounds; researches on dilatation and specific heat of alloys, on capillary phenomena, and on static electricity. No wonder that in the same year (1877) he was appointed to the Professorship in Liége and was elected a corresponding member of the Belgian Academy.

Although Spring showed, especially by his researches on oxygenated compounds of sulphur, his aptitude for inorganic and experi-

W. Spring.

mental chemistry, his mind was much more attracted by the physical side of chemical phenomena, and nearly all his numerous papers, which follow each other with a remarkable "esprit de suite," are concerned with physico-chemical problems. He is to be considered as one of the chief pillars of modern physical chemistry; van't Hoff, whom Spring met in Bonn, was still in the early stage of his career, as were also Ostwald, Arrhenius, and many others of this brilliant school.

In a series of remarkable researches, Spring showed how the action of high pressures changes the physical state and the reactivity of solids; powders become hard masses; some metals become fluid, and solders can be made in that way; many chemical reactions (especially the formation of metallic sulphides) can be brought about by pressure alone. It was Spring who showed that a system under pressure would always assume that physical state the density of which is in accordance with the available volume at the pressure employed. A very ingenious experiment proved that these actions were the result of pressure alone, and not of temperature. A bullet of lead was placed on a mass of phorone, and gradually submitted to a pressure of a few thousand atmospheres; after the experiment the phorone was found to be transformed into a hard mass, with the lead bullet occupying the same position at the top of the phorone, so that at no moment had the temperature reached the melting point of phorone, which is 28° at ordinary atmospheric pressure. The action of pressure was one of the chief ideas that always occupied his mind, and as recently as 1907 he published a new explanation of the "retrogradation" of phosphates.

It is interesting to notice how the work carried out by Spring was never limited to pure physics and chemistry; geological and natural phenomena always attracted his attention at the same time. This is true, not only with regard to his experiments on pressure, but also to numerous others: researches were carried out on the amount of solid matter carried down by a river; on the determination of the conditions influencing the amount of carbon dioxide in the atmosphere; on a new theory of storms; on the colour of the sky, and of natural waters as well as of other liquids.

With the last-mentioned research we reach one of the principal stages of Spring's scientific career; for here one can see how, from the observation of natural phenomena, he could develop one of the most far-reaching problems of physical chemistry. One cannot help recalling here the name of Tyndall, whose experiments on the luminosity of liquids when illuminated by a very strong light were the point of departure of Spring's work in this direction. It will also be worth noticing incidentally that both found in their Alpine holiday trips the subject of these investigations. In both we find the brain of the "Naturforscher," who asks for an explanation where the common mortal does not gain more than an impression, and contents himself with a look of admiration.

One of Spring's greatest achievements was his success in preparing optically transparent liquids, in which the Tyndall phenomenon had completely disappeared, and in making a set of remarkable experiments on the true colour—by transmitted light—of a number of liquids. Only the few privileged persons who have seen him at work in his laboratory—which, as a rule, was a very close sanctuary—can realise the amount of practical difficulties encountered in these researches, and the masterly way in which they were overcome, thanks to his extraordinary manipulative skill.

In another direction Spring transformed the observation of Tyndall's phenomena into a method for arriving at the constitution of solutions and pseudo-solutions. If it was reserved to Siedentopf and Zsigmondy to work out a practical device for the easy observation of these facts through a microscope, and to give a name to the new science, it was Spring in 1899 who made the first experiment in ultramicroscopy.

In 1905 he published a highly interesting experiment on the limit of visibility of a fluorescein solution, which gave him a method for the experimental determination of the highest limit of the weight of molecules and atoms: certainly one of the most ingenious devices ever put forward in regard to an experimental valuation of the smallest particles of which matter is formed.

Pursuing the same idea, he showed that fairly concentrated saline solutions, even when prepared with optically transparent water, show the Tyndall phenomenon: indicating that fairly large aggregates exist there in solution. Spring then introduced us to an entirely new conception of slow changes occurring in solution; he showed (1909) that the same saline solutions gradually become less illuminated when placed in the beam of light, and that some of them become optically transparent after a period of four years. With regard to salts which undergo a certain amount of hydrolysis in aqueous solution, there occurs a noticeable clearing of their solutions after a number of years, showing a retrogradation of the hydrolysis. This fact is also corroborated by the decrease of electrical conductivity, less free acid being present. Certain chemical reactions (as, for instance, esterification) were known to be exceedingly slow and to proceed for years; now we learn that a solid put into water undergoes at first a rough disintegration, but that it takes years to reduce the last aggregates into their ultimate particles.

Very valuable work was also done by Spring on the coagulation of colloidal solutions, both by means of the electric current (cataphoresis) and by electrolytes. Quite recently his researches on the colloidal compounds of soap with charcoal and metallic bases (of iron and aluminium) showed how the rapidity of the coagulation was dependant on the concentration of the electrolyte added; but the phenomenon exhibits an undulatory behaviour, characterised by the presence of different "optima" of concentration.

In the last year of his life, Spring was busy working out a simplified method for the examination of the colour of pure liquids. The very ingenious device on which this is based—and which he discussed with the writer—has not yet been published; but it is to be hoped that it will not be lost to Science.

In a notice like this, which must necessarily be short, it is only possible rapidly to indicate the chief subjects of Spring's scientific activity. In addition to his research work, he wrote a book on the life and work of J. S. Stas; he had a great veneration for the celebrated chemist, and enjoyed his personal friendship. He also edited the complete edition of Stas's works published in 1894, fulfilling this labour of love with that scrupulous care which characterised all his work.

The same solicitude was displayed in matters of less importance, and a good example of it is shown in the numerous reports on papers presented to the Brussels Academy, of which scientific body he was an active member since 1884, the office of President being filled by him during the year 1899.

After a long struggle against apathetic officialdom, he at last was successful in obtaining (1893) the necessary funds for a new Chemical Institute in conformity with the demands of modern science. During two years he had to give up his scientific work entirely, and to devote himself to the erection of the laboratories; more than seventy plans were elaborated, and even designed by himself, so as to spare any interference of an architect. Here, again, he displayed his great practical ability, and even the most minute details were carefully provided for. No wonder, then, that this Institute has since served as model for foreign chemical laboratories.

Amongst the numerous students who attended his lectures, only the very small minority who took degrees in chemistry had any idea of the very high scientific attainments of their professor. He always tried to escape any official recognition of his talents, and displayed the same quality of great modesty on all occasions; he never alluded to himself in his lectures, even when discussing subjects on which he had worked. None of his students will ever forget his marvellous power of exposition, the clearness and logic of his deductions, and the kindness that he showed to each one.

It may perhaps be interesting to recall the tribute of admiration which even geographers paid to him when a new cape discovered in the Antarctic by the de Gerlache expedition was named "Cap Walthère Spring." A deep sense of loss was felt everywhere on the announcement of his premature death; it affected especially the Chemical Society and other scientific bodies which had conferred upon him their honorary membership, amongst which are the Royal Institution and the German Chemical Society. All who have ever met him will probably regret the man even more than the scientist; they will remember his kindness and readiness to render a service, his great love and true sense of justice, his natural wit and humour, combined with the seriousness of all his actions. We have lost a man in the highest sense of the word.

Frédéric Schwers.

NEVIL STORY-MASKELYNE.

Born September 3rd, 1823; Died May 20th, 1911.

The Maskelyne family can be traced back as landowners in Wiltshire to 1435. Edmund Maskelyne (1564–1629) was M.P. for Cricklade in 1625, and the same constituency was also represented by his son, Nevill Maskelyne, in 1660, and again (both before and after its conversion into the Cricklade Division of Wiltshire) by the late Mr. Story-Maskelyne from 1880 to 1892.

The name Nevill or Nevil was borne by many of Edmund's descendants, among whom was the celebrated Astronomer Royal. His only child, Margaret Maskelyne, married in 1819 Mr. Anthony Mervyn Reeve Story, who had taken a Double First at Oxford at the early age of nineteen, and was elected a Fellow of the Royal Society in 1823. Subsequently, Mr. Story, as owner of the Maskelyne estates in right of his wife, took the name of Story-Maskelyne, by which his descendants were thenceforth known.

His eldest son, the subject of this memoir, was born on September 3rd, 1823; was educated at Bruton Grammar School, in Somersetshire; entered Wadham College, Oxford, in 1842; and took his Degree with a Second Class in Mathematics in 1845.

He had been intended by his father for the Bar, and, after leaving Oxford, spent his time between Basset Down, the family place in Wiltshire, and the Temple.

About two years before he went to Oxford, Story-Maskelyne had become known to Dr. Buckland, who visited Basset Down to collect fossils in the great cutting in the Kimmeridge clay made between Swindon and Wootton Bassett during the construction of the Great Western Railway. By him the young man, shortly after his arrival in Oxford, was introduced to Dr. Daubeny, and thus was welcomed to the meetings of the Ashmolean Society, to which, as he believed, he was the only undergraduate then admitted.

During his undergraduate days he studied chemistry, attending Dr. Daubeny's lectures in that subject, Buckland's in mineralogy, and experimenting both in his own rooms and later in a laboratory which he established at Basset Down.

He also formed an early intimacy with Fox-Talbot, and was among the first to practice the art of photography in its then stage of development. At the meeting of the British Association held in Oxford in 1847 he read a short paper on some of his results, and he used to relate that he showed the method of developing a photograph to Faraday, who had never seen the operation performed before. At a later period Maskelyne was recognised as an authority on the early history of photography. An anonymous article on "The Present State of Photography," which appeared in the *National Review* in April, 1859 (No. 16, pp. 365–392, Chapman and Hall), was written by him, and he was Secretary to a Committee which reported to the British Association on the same subject in the same year ("Rep.," 1859, pp. 103–110).

At the meeting of the British Association already referred to (1847) he met Benjamin Brodie, who had just returned to London after completing the Giessen course under Liebig. This new friend, who offered the hesitating recruit an opportunity of working at chemistry in his own laboratory, induced him to give up law and to throw in his lot with science, a decision which was doubtless strengthened by his growing friendship with Faraday. Only three years later, in 1850, Dean Buckland became unable to carry on his work at Oxford, and, to his great surprise, Story-Maskelyne was asked if he would undertake the lectures on Mineralogy which had been delivered by his old friend. With becoming modesty he suggested that Brodie should have been invited in preference to himself, but when Brodie refused the invitation he consulted Faraday as to his own course of action.

"Faraday's answer," he afterwards wrote to Mrs. Gordon, "was, 'Accept the offer, and, as you have several months before you, come here (to the Royal Institution) on such evenings as you may have [free]. You shall have a room and light, and I will get from the library any books you may need.' A noble offer; need I say that I accepted it?"

His acceptance of the Oxford post was, however, subject to the condition that a laboratory should be assigned to him where he could teach Mineralogical Analysis and Chemistry in general. In answer to this request a suite of rooms was allotted to him, situate under the Ashmolean Museum, and comprising six living rooms and offices, a laboratory, and a small theatre. There he lived from 1851 to 1858.

During his residence in Oxford, Story-Maskelyne served as Secretary of the Ashmolean Society, and published various papers, among which may be mentioned that "On the Oxidation of Chinese Wax" (*Chem. Soc. Journ.*, 1853, **5**, 24–26), and an "Investigation on the Vegetable Tallow from a Chinese Plant (*Stillingia sebifera*)" (*Chem. Soc. Journ.*, 1856, **7**, 1–13; Erdmann's *Journ. Prakt. Chemie*, vol. 65, 1855, pp. 287–296).

In addition to his scientific work Story-Maskelyne took an active part in the historic struggle for the erection of a museum in Oxford, and was Secretary to the first Delegacy to which the museum question was entrusted.

In 1855 Sir Benjamin Brodie was appointed Professor of Chemistry at Oxford, and Story-Maskelyne, who was successively Deputy Reader, Reader, and Professor of Mineralogy, held also for a short time the title of Assistant Professor of Chemistry. By Brodie's appointment, however, as Maskelyne himself said, his own Chemical Laboratory became "redundant" as a University Institution. The difficulty was soon solved, for within the next two years he was appointed to the newly-established post of Keeper of the Minerals at the British Museum, in which, perhaps, the chief work of his life was done.

He continued to hold the Chair of Mineralogy at Oxford, and by inviting the most promising of his pupils to work with him in London he extended the usefulness of both offices, and trained the next generation of British mineralogists. Among the best known of these are W. J. Lewis, the Professor of Mineralogy at Cambridge; Lazarus Fletcher, who succeeded him as Keeper of the Minerals, and is now Director of the Natural History Museum at South Kensington; and Sir Henry Miers, who followed him as Professor at Oxford, and is now Principal of the University of London.

To these may be added Dr. Viktor von Lang, who, after studying for two years in the British Museum, was successively Professor of Physics at Grätz and Vienna, and was associated with Joseph Grailich in a series of Memoirs on "Crystallography," published in the *Sitzungsberichte* of the Academy of Vienna.

On settling in London Mr. Maskelyne married a lady who was herself a member of a scientific family, being granddaughter of Dillwyn, the well-known botanist, and daughter of Mr. John Llewelyn, of Penllergare, Swansea, who was a Fellow of the Royal Society.

For six years previous to 1857 there had been no one at the British Museum who took any special interest in Mineralogy, and it was only in that year that the special Department of Mineralogy was instituted, and Story-Maskelyne was appointed Keeper. For five years he had only one assistant, the late Mr. Thomas Davies, who came without any special training, but, fortunately, developed an extraordinary capacity for museum work, acquired an unrivalled eye-knowledge of minerals, and became a most valuable scientific assistant.

Maskelyne undertook the whole rearrangement of the collection according to the crystallo-chemical system of Rose. He busied himself much with the acquisition of specimens, and, under his direction, the collection was enormously increased and improved. He was quick to see the importance of making as complete a collection of meteorites as possible, and devoted a great deal of his time and energy to their study.

There was at that time no laboratory or equipment for scientific research. Gas was not allowed in the building, and it was therefore extremely difficult to conduct any real scientific investigation. Maskelyne's work was during these years very largely confined to what could be done with the microscope and goniometer. He was one of the first to investigate thin sections of rocks and minerals with the aid of polarised light, and was actually using a microscope, with a revolving stage and eyepiece micrometer, for the study of thin sections of meteorites, about the year 1861.

By 1867 he had made it clear to the authorities that scientific research could not be carried on without a chemical laboratory, and in that year Dr. Flight was appointed as assistant, and the laboratory was fitted up in a house outside the Museum.

Maskelyne held the office of Keeper of Minerals from 1857 to 1880, and, during that period, was able, not only to maintain and develop the collections, so that they became the largest and best arranged series of minerals and meteorites in existence, but also to issue, with the help of his assistants, an important series of scientific memoirs.

Among these especially noteworthy are the series of "Mineralogical Notes" published in 1863–4, in conjunction with von Lang, and the "Mineralogical Notices" published in 1871–4, in conjunction with Flight.

A survey of Maskelyne's published papers shows that, up to 1855, he was chiefly interested in chemical problems, that the study of meteorites engaged his attention as soon as he went to the British Museum, and that the period of his greatest scientific activity, as a mineralogist, judged by the published papers on minerals and meteorites, ranged from 1860 to 1880.

Among the more important of the papers on meteorites may be mentioned the investigations on the Parnallee, Nellore, Breitenbach, Manegaum, Busti, Shalka, and Rowton meteorites; among mineral researches, those upon Langite, Melaconite, Tenorite, Andrewsite, Connellite, Chalkosiderite, and Ludlamite.

New minerals described by him were Andrewsite, Langite, Liskeardite, and Waringtonite, and the following constituents of meteoric stones were first isolated and determined by him: Asmanite, described in 1871 as an orthorhombic variety of silica from the Breitenbach meteorite isomorphous with Brookite, but now generally regarded as identical with the mineral Tridymite, described by vom Rath in 1868; Oldhamite, a calcium sulphide, described in 1862, from the Busti meteorite; and Osbornite, described in 1870, from the same stone. He was also the first to recognise the presence of Enstatite in meteorites.

He was always much interested in the history of the diamond, and, in a paper published in *Nature* in 1891, returned to the history of the Koh-i-noor, on which he had first written in 1860. There was considerable stir about 1880, just before he left the Museum, concerning the artificial production of the diamond; Maskelyne proved that the supposed diamonds which had been manufactured by Mactear were in reality a crystallised silicate.

The mode of occurrence of the diamond in South Africa also occupied his attention, and he described the Enstatite rock, which is associated with it in that part of the world.

Maskelyne's views on Crystallography were first made public in a series of lectures delivered before the Chemical Society in 1874, and more fully in his well-known text-book, "The Morphology of Crystals," which was published in 1895. In this, as in his University lectures, the attention of students was especially called to the important subject of symmetry. From his early days this had particularly engaged Maskelyne's attention, and many of his views are no doubt the result of discussions between him and Viktor von Lang at the time when the latter was Assistant in the Mineral Department, from 1862–4. Von Lang's book, which was published in 1866, treated the subject of crystal symmetry in a novel and original manner, and Maskelyne's publications were devoted to the development of this subject on somewhat similar lines. His "Morphology of Crystals" was published at so late a date that other methods of treatment, and another nomenclature, had become somewhat firmly established before it appeared. Had it been published when first written, it would have attracted much attention as a highly original work. Some of the proof-sheets were in the hands of his pupils for very many years before the book ultimately appeared; his views had been made known to them throughout the whole period of his professional career, and profoundly influenced their own teaching.

The chief feature of this book is the investigation of the geometrical relations of a crystalloid system of planes, that is to say, planes obeying the law of rational indices, and the most important and original part of the investigation is that which deals with the varieties of symmetry possible in such a system. The subject is developed by a study of the symmetry planes inherent in the system; the important proof concerning the number of symmetry planes possible in a crystalloid system and their mutual inclinations was, it is stated by Prof. Lewis in his "Crystallography," given in a course of lectures by Prof. Maskelyne as far back as 1869.

In his mathematical, as in his scientific writings, Maskelyne's work was characterised by a remarkable distinction and charm of style, which was, indeed, part of his character, and prevailed in everything that he undertook. In all his scientific work the mind and sympathies of an artist declared themselves, and were as well known to his pupils as to his personal friends.

It was therefore characteristic that his devotion to his work as Keeper of Minerals did not lead him to narrow the range of his interests to mere specialism, but to extend it to a kindred subject. A good deal of his scientific work brought him into contact with ancient art, for which he always had a great fondness, and which was fostered by his opportunities in the British Museum. But though favourable circumstances undoubtedly stimulated him, his taste was shown both before and long after he was connected with the Museum. As far back as 1869, for example, he was discussing at the Societies of Antiquaries the nature of the Murrhine vases of the ancients, which he believed to be composed of heated sard, in opposition to Westrop, who thought Pliny's Murrhina to be fluor. As late as 1894 he was lecturing in Wiltshire upon the subject of Greek art. In the intervening years he not only formed a very valuable private collection of antique gems, but, at the request of the Duke, produced the well-known catalogue of the engraved gems belonging to the Duke of Marlborough's collection.

A great change took place in Maskelyne's life on the death of his father in 1879. Henceforth he became an active country gentleman, though he continued to hold his office of Professor of Mineralogy at Oxford. At that date funds were not available for securing the whole time of a resident professor, and it was in the interests of the University itself that he retained office while waiting for the adequate endowment of his Chair. So soon as this was secured, by attaching the professorship to the Waynflete foundation at Magdalen College, he retired.

In 1880 he was elected in the Liberal interest as Member for Cricklade, and thereafter sat in three Parliaments, that is, until 1892. Although he could hardly be called a conspicuous, he was unquestionably an active, Member of Parliament. He was one of the Liberals who refused to follow Mr. Gladstone in his Home Rule policy, and without any doubt or hesitation ranged himself from the first among those who threw out the Bill of 1886. His constituency, nevertheless, returned him again to Parliament in the General Election which followed. His interest in politics did not flag after his defeat in the election of 1892, and was enhanced by the career of his son-in-law, the late Mr. Arnold-Forster.

He also took an active part in county matters, was a Member of the Wiltshire County Council from its foundation till he was over eighty years of age, and was for many years Chairman of the Agricultural Committee. He was an active Member of the Bath and West of England Agricultural Society, the presidency of which he declined, on account of his advanced years, when the meeting was held in Swindon. It was at his suggestion that the first itinerant dairy school was established.

In 1904 Mr. Maskelyne underwent a severe operation, and from that time until his death in 1911 he was always more or less of an invalid. His old age was, however, brightened by his intense mental activity and by his interest in the progress of science. In 1904, when his life was in great danger, he exclaimed: "I must live, I want to know more about radium."

He was a good scholar, and was one of the few scientific men who read Homer until late in life. The variety of his interests had brought him into contact with many of the most distinguished minds of two generations. He knew the bearers of all the best known Oxford names. He helped to entertain Liebig when he visited that University. He was the intimate friend of Charles Mansfield, the chemist, who died too young to have achieved a great popular name, but whose heroic end in a laboratory accident he could not recall without emotion. With him he worked in the social movement associated with the names of Kingsley and Maurice, and frequently lectured at the Working Men's College. At the British Museum he was visited by many foreign mineralogists and collectors of minerals and gems. As a Member of Parliament he was on terms of friendship with Mr. Chamberlain and many other politicians. His wide knowledge of men and things, his memories of a long-distant past, and his keen attention to the problems which are interesting the youth of to-day, made him a delightful companion to young and old.

To use his own words, "the twilight of his departing day" was cheered by the consciousness of having lived through a great age and by the pleasure of having "known, in different degrees, so very many of the vigorous men to whom that era is indebted for its splendour."

Mr. Story-Maskelyne was the recipient of many testimonials to his scientific worth. He was an Honorary Fellow of Wadham College, and received in 1902 the Honorary Degree of Doctor of

Science from the University of Oxford. He became a Fellow of the Royal Society in 1870, served twice on the Council, and was Vice-President from 1897 to 1899. He was Corresponding or Honorary Member of the Imperial Mineralogical Society of St. Petersburg, of the Society of Natural History of Boston, of the Royal Academy of Bavaria, and of the Academy of Natural Sciences in Philadelphia.

Mrs. Maskelyne and his three daughters survive him. One of the latter married the late Right Hon. H. O. Arnold-Forster, some time Secretary of State for War, and another is the wife of Sir Arthur Rücker.

A. W. R.
H. A. M.

LOUIS JOSEPH TROOST.*

BORN, 1825; DIED, SEPTEMBER 30TH, 1911.

BY the death of Troost, on September 30th, at the ripe age of eighty-five, France loses the last surviving member of that group of workers—pupils of Henri Sainte-Claire Deville at the École Normale—who created, mainly under his inspiration and leadership, what was practically a new department of chemical science. Thermal chemistry, as we understand it to-day, may be said to have originated in mid-Victorian times. It may be urged that the relations of chemistry to heat are so intimate that the study of these relations is necessarily as old as the study of chemistry itself. But it was only at the beginning of the latter half of the last century that the subject of thermal chemistry was attacked. Systematically, and for the most part in France, at the instigation of Deville, who, with the aid of Troost, Debray, Isambert, Hautefeuille, and Ditte, laid the foundations of that imposing superstructure to which this special department of knowledge has now attained.

Troost, who was born in 1825, was educated at the Lycée Charlemagne. He entered the École Normale in 1848, becoming an assistant there in 1851, and receiving his doctorate of science in 1857. For some time he taught in the provinces, but ultimately took charge of the chair of chemistry at the Lycée Bonaparte at Paris, and then, in 1868, became Maître de Conférences at the École Normale. In 1874 he became a professor in the faculty of sciences of Paris, where he remained until 1900, when he retired. In 1884 he succeeded Wurtz at the Academy of Sciences. For many years he was a commander of the Legion of Honour.

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* Reprinted, by permission, from *Nature* (Oct. 12th, 1911).

Troost was an indefatigable experimentalist and a prolific writer. His published memoirs, either alone or in association with Deville, Marie-Davy, and Hautefeuille, number close upon a hundred. His earliest essays were in pure inorganic chemistry: he prepared and studied the salts of lithium, which, in the middle of the nineteenth century, was regarded as a rare element. By the student, however, Troost is mainly remembered by reason of his work with Deville on the determination of vapour densities at high temperatures, the study of which had received an enormous impetus on account of the applications of the doctrines of Avogadro and Ampère. The values so obtained have become classical, and are to be found in practically every systematic treatise of chemistry. With Deville, he largely developed the conception of dissociation, and his memoir on the vapour density of chloral hydrate gave rise to a memorable controversy on the value of volumetric considerations in the determination of equivalents. In conjunction with Hautefeuille he followed Debray in elucidating the laws governing dissociation, the recognition of the fundamental phenomena of which we owe to Deville. In this connexion we may cite the memoirs on the conditions determining the absorption of hydrogen by palladium, potassium, and sodium, the dissociation of the sesquichloride of silicon, and the transformations of cyanogen into paracyanogen, and of cyanic acid into cyanuric acid. With Deville he studied the porosity of metals at high temperatures, and with Hautefeuille the solubility of gases in metals.

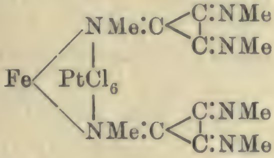
Troost was a frequent contributor to metallurgical chemistry, and made important contributions to our knowledge of the parts played by silicon and manganese in determining the physical properties of the various forms of commercial iron. His treatise of chemistry, which originated out of his connexion with the Sorbonne, has gone through innumerable editions, and for many years past has been a standard text-book to successive generations of pupils.

Troost, in spite of his advanced years, enjoyed excellent health up to a short time before his death. He preserved his faculties practically unimpaired, and was active and industrious to the last on the numerous commissions in which he took part, and more particularly on the Commission des Inventions at the Ministry of War, of which he had been president for some years past.

LXXIV.—*The Alkylation of the Ferro- and Ferricyanides.*

By Ernald George Justinian Hartley.

In two recent communications (Trans., 1910, **97**, 1066, 1725) the author described some new derivatives of hydroferrocyanic acid formed by the action of anhydrous potassium ferrocyanide on methyl sulphate. There were thus obtained several salts of a base, $(CH_3)_6FeC_6N_6(OH)_2$, which was too unstable to exist in the free state; for example, the acid sulphate had the composition $(CH_3)_6FeC_6N_6SO_4,H_2SO_4$. From the latter was prepared, amongst other derivatives, a characteristic insoluble platinichloride, which was found to be most useful for identifying these salts. Finally, tetramethyl ferrocyanide was obtained. In a subsequent paper on the constitution of these compounds (Trans., 1911, **99**, 1549) it was shown that the methyl groups are all directly attached to nitrogen, and a formula similar to that suggested by Browning (Trans., 1900, **77**, 1238) was adopted to represent their constitution, thus:



for the platinichloride.

It was thought interesting to ascertain whether ferricyanides would behave in a similar way, and experiments were carried out exactly as before, but substituting potassium ferricyanide for the ferrocyanide. The former reacted with methyl sulphate at 100° with much decomposition, a large quantity of some compound of the nature of Prussian blue being formed. On filtering the liquid portion of the mixture from the solid matter and distilling off the excess of methyl sulphate under diminished pressure, a crystalline residue was left, which proved to be exactly the same as that produced when the ferrocyanide was used, namely, a mixture of the above-mentioned acid sulphate and the neutral methosulphate, $(CH_3)_6FeC_6N_6(SO_4{\cdot}CH_3)_2$.

It is evident, therefore, that under these conditions some reducing action takes place, and that it is not possible in this way to obtain a methylated ferricyanogen derivative. Owing, however, to the extremely poisonous properties of methyl sulphate, no further experiments were made to determine the exact nature of the reduction.

The reaction between alkyl iodides and silver ferro- and ferri-cyanides was next investigated. Freund (*Ber.*, 1888, **21**, 931) first prepared tetraethyl ferrocyanide by this method, but he gives no details as to the amount of product. Browning (*loc. cit.*) repeated his experiments, and states that he obtained a very bad yield, a result which the author has also experienced when the preparation was carried out as far as possible according to Freund's paper. Since it appears that a reaction of this nature should take place fairly completely, a further study of the process was undertaken. The substances used for the first experiments were silver ferrocyanide and methyl iodide with a view to obtain tetramethyl ferrocyanide, since the properties of the methylated ferrocyanogen derivatives were more familiar to the author than those of the corresponding ethyl compounds. Five grams of dry powdered silver ferrocyanide were heated with 10 c.c. methyl iodide in a sealed tube at about 95° for six hours. On cooling it was seen that the solid matter had altered in appearances, and consisted largely of a grey, crystalline powder. The excess of methyl iodide was filtered off, and on evaporation left only a trace of a dark brown substance. The solid crystalline portion when dried weighed 11·4 grams, which corresponds very closely with an addition of six molecules of methyl iodide to each molecule of silver ferrocyanide. Since a previous experiment had shown that tetramethyl ferrocyanide combines very readily with methyl iodide to form hexamethylferrocyanogen iodide, $(CH_3)_6FeC_6N_6I_2$, when the two are heated together in a sealed tube as above, it was at first concluded that silver iodide and this hexamethylated compound had been produced in this case. The crystalline matter was therefore first digested with chloroform in order to dissolve any of the tetramethyl compound, if present, when only a very small amount of the above brown substance was extracted; afterwards it was heated with methyl alcohol, which has been found to dissolve hexamethylferrocyanogen iodide quite readily. In this case, however, only a further small quantity of the same brown-coloured matter was removed.*

It thus seemed probable that the substance was a compound of silver iodide with hexamethylferrocyanogen iodide, especially as it appeared under the microscope to consist of a homogeneous crystalline powder. This was subsequently confirmed, when it was found that the double salt is decomposed by digestion with warm dilute nitric acid into silver iodide and hexamethylferrocyanogen nitrate; for example, in one experiment 2·120 grams were gently warmed with nitric acid until the insoluble matter had become entirely yellow. The silver iodide when washed and dried weighed 1·350 grams, the calculated amount being 1·331 grams, assuming the double salt to be $(CH_3)_6FeC_6N_6I_2,4AgI$. In some experiments where the reaction had not been so complete, some unchanged silver ferrocyanide could be seen mixed with the silver iodide. On evaporating the filtrate from the silver iodide to dryness, a crystalline mass was left. This was dissolved in ethyl alcohol, and to the solution concentrated sulphuric acid was added, when an acid sulphate was precipitated the identity of which as a hexamethylferrocyanogen salt was definitely confirmed by a microscopic examination of the platinichloride.

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* This brown substance, of which only a fraction of a gram was formed, contained iron, carbon, nitrogen, and iodine. It is identical in its properties with the dark crystalline compound described later in this paper in the section on ferricyanides.

A second method of decomposing the double salt consists in digesting it with a warm solution of silver nitrate, when the same nitrate as above passes into solution, and the silver iodide is all separated according to the equation:

$$(CH_3)_6FeC_6N_6I_2,4AgI + 2AgNO_3 = (CH_3)_6FeC_6N_6(NO_3)_2 + 6AgI.$$

In carrying out the above reaction between silver ferrocyanide and methyl iodide, a large excess of the latter was used in order that the silver salt should be completely covered with liquid. Some experiments were subsequently made, in which the proportion of methyl iodide to the silver salt was rather less than four molecules to one, and the former was mixed with an indifferent solvent (ethyl alcohol and carbon tetrachloride), so as to bring it in contact with the salt, but in neither case was any trace of tetramethyl ferrocyanide found, although when ethyl alcohol was employed the reaction was somewhat complicated, a considerable amount of hydrocyanic acid being produced and a double cyanide of hexamethylferrocyanogen and silver, soluble in chloroform, was isolated in small quantity. In the main, however, the reaction appeared to be the same as when excess of methyl iodide was taken, but, of course, in this case a considerable proportion of the silver ferrocyanide was unacted on.

The reaction between silver ferricyanide and methyl iodide was next investigated. 3·05 Grams of the silver salt were heated with 7 c.c. of methyl iodide for seven hours at 95° in a sealed tube. The solid matter had thereby been converted into a crystalline powder very similar to that formed when the ferrocyanide was used, but in addition to the grey crystals there were seen to be numerous dark brown plates and needles, many with an iodine-like lustre. After filtering and drying, the solid portion weighed 7·51 grams, which again corresponds with an addition of nearly six molecules of methyl iodide to each molecule of the silver salt. The brown crystals were found to be only sparingly soluble in alcohol, but very soluble in hot acetone. The whole of the solid matter was therefore extracted with this solvent, when a dark brown solution was obtained, which deposited the substance in almost black crystals on evaporation. The total amount of this substance, including the part extracted with alcohol and a small quantity left on evaporation of the excess of methyl iodide, was 1·24 grams. The portion of solid matter insoluble in acetone now appeared under the microscope to consist of homogeneous crystals. When treated either with nitric acid or silver nitrate in the same way as the previously described ferrocyanide, this salt also was decomposed into silver iodide and a crystalline nitrate, which proved to be the same as that obtained from the ferrocyanide, namely, hexamethylferrocyanogen nitrate. This was confirmed by conversion of the nitrate into the acid sulphate, in which the iron and SO_4 were determined (Found, Fe = 11·11 and 11·42. Calc., Fe = 11·23; SO_4 = 38·24. Calc., 38·68 per cent.), and into the characteristic platinichloride.

2·188 Grams of the double salt after digestion with dilute nitric acid gave 1·385 grams of silver iodide, which corresponds with the formula $(CH_3)_6FeC_6N_6I_2,4AgI$, the calculated amount being 1·374 grams.

The dark crystalline substance deposited from acetone was next examined. It was slightly contaminated with some oily matter, from which it was not found possible to free it entirely. It loses no weight at 100°, but on further heating it evolves iodine, and on strong ignition leaves a residue of ferric oxide, but no silver. When boiled with potassium hydroxide an alkaline vapour is evolved, accompanied by a strong odour of *iso*cyanides. It contains no free iodine, since it is altogether insoluble in carbon tetrachloride, and only sparingly so in chloroform or alcohol, forming a brown solution in both cases. It is insoluble in water, but on treatment with a solution of silver nitrate it is rapidly decomposed, even in the cold, a strongly acid solution resulting, and a mixture of silver iodide and iodate being precipitated. On filtering and removing the excess of silver with hydrochloric acid and evaporating to dryness, a crystalline residue is left, which is soluble in alcohol. A few drops of concentrated sulphuric acid added to this solution produce a crystalline precipitate, which can be identified as a hexamethylferrocyanogen salt by conversion into the platinichloride. These properties show pretty conclusively that the substance is a hexamethylferrocyanogen periodide, in which a part of the iodine is somewhat loosely held and reacts with silver nitrate in the same way as free iodine, forming silver iodide and iodate and nitric acid. A determination of iodine agrees fairly well with the number required for the formula $(CH_3)_6FeC_6N_6I_6$, considering that the substance could not be obtained in a perfectly pure condition:

0·2274 gave 0·2918 AgI. I = 69·3.

$C_{12}H_{18}N_6I_6Fe$ requires I = 71·5 per cent.

In order to verify the composition of this compound, a small quantity was prepared synthetically. 0·32 Gram of pure tetramethyl ferrocyanide was heated with excess (0·7 gram) of iodine and 4 c.c. of methyl iodide in a sealed tube at 105° for six hours. On cooling it was seen that the solid matter consisted entirely of dark crystals, completely resembling the above periodide, both in appearance and properties. After washing away the excess of iodine with carbon tetrachloride, the crystals weighed 1·23 grams, the calculated weight, assuming the above formula, being 1·25 grams.

A determination of the iron and iodine gave the following numbers:

0·4741 gave 0·0363 Fe_2O_3. Fe = 5·36.
0·2551 „ 0·3373 AgI. I = 71·4.

$C_{12}H_{18}N_6I_6Fe$ requires Fe = 5·27; I = 71·5 per cent.

The reaction between silver ferricyanide and methyl iodide can now be expressed by the following equations:

$$\text{(i)}\ Ag_3FeC_6N_6 + 6CH_3I = (CH_3)_6FeC_6N_6I_2 + 3AgI + I.$$

The ferricyanide is here reduced to ferrocyanide by the methyl iodide with liberation of iodine. The hexamethylferrocyanogen iodide then combines partly with the silver iodide and partly with the free iodine, and the complete equation can be written:

$$\text{(ii)}\ 4Ag_3FeC_6N_6 + 24CH_3I = 3(CH_3)_6FeC_6N_6I_2,4AgI + (CH_3)_6FeC_6N_6I_6.$$

It would appear probable from these experiments that ferricyanogen derivatives similar to the methylated ferrocyanogen compounds cannot be obtained, and since the production of such alkylated ferricyanides was the main object of this research, it was not considered worth while to carry on this work much further. It may, however, be mentioned that one or two experiments carried out with silver ferrocyanide and ethyl iodide show that under similar conditions the reaction is not so complete as with methyl iodide. A small quantity of tetraethyl ferrocyanide was usually formed, and also a double silver salt, the properties of which resembled those of the corresponding methyl compound.

Preliminary experiments on the reaction between silver cobalticyanide and methyl iodide show that this salt behaves quite differently from the ferricyanide. It is hoped that it will shortly be possible to lay these results before the Society.

This work has been carried out in Lord Berkeley's laboratory, to whom the author's best thanks are due.

FOXCOMBE LABORATORY,
NR. OXFORD.

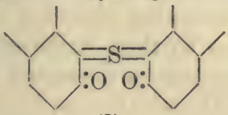
LXXV.—*Some Reactions of β-Naphthasulphonium-quinone.*

By HAROLD CHRISTOPHER and SAMUEL SMILES.

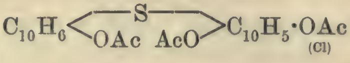
THE experiments which are described in this paper were made during a study of the behaviour of dehydro-β-naphthol sulphide, or, as it may be more correctly termed, the β-naphthasulphonium-quinone (Trans., 1911, **99**, 977), which is obtained by gently oxidising β-naphthol sulphide. The hope was entertained that the results would indicate the points of resemblance and contrast between this and other quinones, particularly with β-naphthaquinone, the closest analogue in the oxygen series. In previous investigations (Henriques, *Ber.*, 1894, **27**, 2993; Hilditch and Smiles, *loc. cit.*) attention has been drawn to the products of reduction, to the oxidising power, and to the formation of a diphenylhydrazone of this substance.

Of all the numerous reactions which are exhibited by quinones, perhaps the more interesting are those induced by a set of reagents such as acetyl chloride or hydrogen chloride and acetic anhydride in presence of sulphuric or camphorsulphonic acids. These have been applied to quinones as general reagents with remarkable results (Schultz, *Ber.*, 1882, **15**, 652; Thiele, *Ber.*, 1898, **31**, 1247; *Annalen*, 1900, **311**, 341), and it may be recalled that they furnish the acetyl derivatives of trihydroxy- or of chlorodihydroxy-compounds, in which two hydroxyl groups are formed by reduction of the quinonoid system; thus *p*-benzoquinone yields 1:2:4-trihydroxybenzene or chloroquinol, whilst the naphthaquinones behave in a similar manner.

From these data it is nevertheless impossible with confidence to predict the behaviour of β-naphthasulphonium-quinone, for this contains a quinonoid system of unique type (I); but it might be considered probable that the products would be chloro- or acetoxy-derivatives of the sulphide (II). Experiments, however, have shown that derivatives of naphthathioxin (III) are obtained, acetyl chloride or hydrogen chloride yielding chloronaphthathioxin, whilst

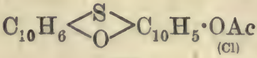


(I).



$$C_{10}H_6<\genfrac{}{}{0pt}{}{\text{———S———}}{OAc\quad AcO}>C_{10}H_5\cdot \underset{(Cl)}{OAc}$$

(II.)

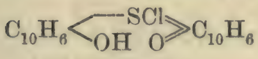


$$C_{10}H_6<\genfrac{}{}{0pt}{}{S}{O}>C_{10}H_5\cdot \underset{(Cl)}{OAc}$$

(III.)

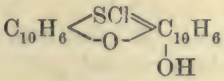
acetic anhydride and camphorsulphonic acid give acetoxynaphthathioxin. The formation of these substances is evidently due to some complex interaction, such as that suggested to explain the characteristic behaviour of di-*o*-hydroxysulphoxides of the aromatic series (Hilditch and Smiles, Trans., 1911, **99**, 974) or the formation of naphthathioxin by the interaction of alkaline reagents with this quinone. In offering the following explanation of this peculiar behaviour, it may be remarked that, although somewhat complex, it is the simplest obtainable, and that the changes involved are justified by independent observations with other substances of like character.

In accordance with the observations and theories of Thiele (*Annalen*, 1889, **306**, 132) and many others, it is assumed that addition of the halogen acid takes place at the quinonoid system, as shown in formula (IV), but previous experience with aromatic



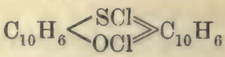
$$C_{10}H_6<\genfrac{}{}{0pt}{}{\text{——SCl}}{OH\quad O}\geqslant C_{10}H_6$$

(IV.)



$$C_{10}H_6<\genfrac{}{}{0pt}{}{SCl}{\text{-O-}}>\underset{\underset{OH}{|}}{C_{10}}H_6$$

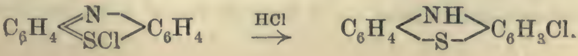
(V.)



$$C_{10}H_6<\genfrac{}{}{0pt}{}{SCl}{OCl}\geqslant C_{10}H_6$$

(VI.)

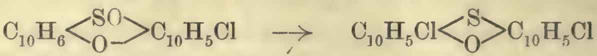
o-hydroxysulphoxides has indicated that substances of this type are unstable in presence of acids, and tend by intramolecular change to pass into cyclic derivatives, such as that represented (V). Now from the extensive work of Kehrmann on cyclic substances containing the ortho-quinonoid arrangement it is clear that this product is the pseudo-base of the thio-oxonium salt (VI), which would be formed in presence of excess of hydrogen chloride. A clue to the final stage of this interaction is found in the behaviour of other cyclic *o*-quinonoid compounds in presence of acid. Experiments have shown (Page and Smiles, Trans., 1910, **97**, 1112) that the chlorides of phenazothionium are attacked by excess of the warm halogen acid, and are then converted into chloro-derivatives of the reduced complex; thus phenazothionium chloride gives chlorothiodiphenylamine:



$$C_6H_4\leqslant\genfrac{}{}{0pt}{}{N-}{SCl}>C_6H_4 \xrightarrow{HCl} C_6H_4<\genfrac{}{}{0pt}{}{NH}{-S-}>C_6H_3Cl.$$

Moreover, a similar interaction has been recently observed in the series of thianthren (Fries and Vogt, *Annalen*, 1911, **381**, 312). There is therefore some justification for assuming that the thio-oxonium derivative, which is of similar type to these azothionium and dithionium compounds, would in like manner be converted into the chloronaphthathioxin (III). The general resemblance between the series of phenothioxin and thiodiphenylamine has been already pointed out (Hilditch and Smiles, Trans., 1911, **99**, 411), but, in order to strengthen the analogy employed in the present argument, further experiments have been made with derivatives of naphthathioxin.

It appears to be characteristic of many of the members of this series that they are oxidised by concentrated nitric acid (D 1·4) without undergoing nitration, the products being the corresponding sulphoxides (VII) (compare thiodiphenylamine, Bernthsen, *Annalen*, 1885, **230**, 116). The latter exhibit the characteristic behaviour observed with the unsubstituted oxides of thiodiphenylamine (Page and Smiles, *loc. cit.*; Barnett and Smiles, Trans., 1909, **95**, 1253) and of thianthren (Fries and Vogt, *loc. cit.*), for they are converted by warm hydrochloric acid into the chloronaphthathioxins (VIII):

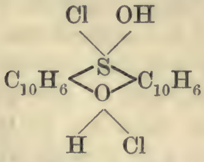


$$\mathrm{C_{10}H_6}<\genfrac{}{}{0pt}{}{\mathrm{SO}}{\mathrm{O}}>\mathrm{C_{10}H_5Cl} \longrightarrow \mathrm{C_{10}H_5Cl}<\genfrac{}{}{0pt}{}{\mathrm{S}}{\mathrm{O}}>\mathrm{C_{10}H_5Cl}$$

(VII.) (VIII.)

The unsubstituted oxide of naphthathioxin furnishes a mixture of chloro-derivatives which are not easy to separate (compare thiodiphenylamine, Page and Smiles, *loc. cit.*), and have not been closely investigated; but the monochloro-derivative (VII) yields the theoretical amount of the dichloro-compound (VIII).

It must be admitted that no direct evidence can be at present adduced to show that the thio-oxonium salt is here formed at an intermediate stage. All that can be said on this question is that the sulphoxide salts, which are formed (Trans., 1909, **97**, 186, 1559; 1911, **99**, 151) prior to the conversion of the thionyl into the quinonoid sulphonium structure, are here capable of existence, for the nitrate of naphthathioxin oxide may be isolated as a fairly stable substance. Hence there is no reason to doubt that the hydrochloride is formed in the initial stage of interaction between the halogen acid and naphthathioxin oxide; but, according to the previous study of this type of change, the essential product from which water is eliminated to form the quinonoid salt must here be the dihydrochloride; and it is very doubtful whether a substance of this nature would be formed under the conditions suitable for this interaction. As an alternative it is possible that chlorination



takes place with the aid of free chlorine or hypochlorous acid liberated from the sulphoxide salt. It may be here observed that the interaction between sulphuric acid and these oxides of naphthathioxin in cold acetic acid solution yields highly coloured, crystalline substances, which are probably the thio-oxonium salts, but unfortunately their stability is not sufficient to enable this conclusion to be supported by accurate analysis. Apart from this question it is clear that the occurrence of the chlorinating process in the naphthathioxin series gives emphasis to the general resemblance between these substances and the derivatives of thiazine; and the assumption made to explain the final stage of the interaction discussed in this paper is somewhat strengthened.

In subsequent paragraphs the reduction of β-naphthasulphonium-quinone with sodium ethoxide is described; the product is the sulphide of β-naphthol (m. p. 212°), from which the quinone was prepared by oxidation. It is noteworthy that Henriques (*loc. cit.*) has observed the formation of an isomeric sulphide of β-naphthol (m. p. 153°) in the reduction of the quinone with acid reagents, and he has also shown that this is converted by alkaline reagents into the normal sulphide of higher melting point. These observations have now been confirmed, and it may be remarked that the different results of alkaline and acid reduction are thus easily interpreted.

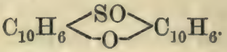
Experiments are now being made to discover the relations between these isomeric sulphides, and the results will be soon published.

EXPERIMENTAL.

Naphthathioxin, $C_{10}H_6\genfrac{<}{>}{0pt}{}{S}{O}C_{10}H_6$.

The preparation of this substance (Mauthner, *Ber.*, 1906, **39**, 1340) by heating the sulphide of β-naphthol in xylene with phosphoryl chloride is not always satisfactory, the yields being poor, and the removal of impurities not easy to accomplish; but by employing tetrachloroethane instead of xylene as the solvent the yields are relatively good (45—50 per cent.), and the product is readily obtained in the pure condition. The preparation was conducted as follows: Twenty grams of β-naphthol sulphide and an equal weight of phosphoryl chloride were dissolved in 300 c.c. of tetrachloroethane, and the solution was heated at 105—110° for three hours. The solvent was then removed by a current of steam, and the residue triturated with a cold aqueous solution of alkali hydroxide. The portion insoluble in this reagent consisted of almost pure naphthathioxin (9 grams), which was identified in the usual manner.

Naphthathioxin Oxide,



$$C_{10}H_{6}{<}\begin{matrix}SO\\-O-\end{matrix}{>}C_{10}H_{6}.$$

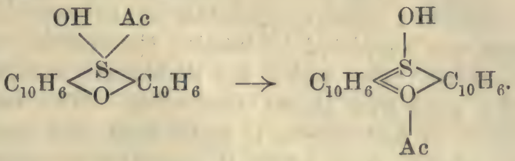
Various reagents have been employed for preparing this substance (Mauthner, *loc. cit.*; Hilditch and Smiles, Trans., 1911, **99**, 415) by oxidation of naphthathioxin, but these are inferior to nitric acid, which furnishes quantitative yields of the almost pure substance. Naphthathioxin was triturated with an excess of nitric acid (D 1·4), and the mixture was then set aside for three hours at the atmospheric temperature. Finally, it was mixed with water, and the precipitated oxide was collected. This was purified by recrystallisation from acetic acid (m. p. 219°. Found, C=75·6; H=3·8. Calc., C=75·9; H=3·8 per cent.). The *nitrate* of *naphthathioxin oxide* may be prepared by adding concentrated nitric acid (D 1·4) to a warm solution of naphthathioxin in acetic acid. On cooling the solution, the nitrate of the base is precipitated as a mass of interlaced needles. These were recrystallised from acetic acid containing a little nitric acid, and then dried over alkali hydroxide in a vacuous desiccator. The nitric acid was estimated by decomposition with standard alkali hydroxide.

Found: $HNO_3=17·04$.

$C_{20}H_{12}O_3S,HNO_3$ requires $HNO_3=16·63$ per cent.

The substance melts and decomposes at 177°; it is not very stable, being partly decomposed by cold ether or by cold water.

When a few drops of sulphuric acid are added to a solution of naphthathioxin oxide in acetic acid, a crystalline precipitate of green needles is obtained. This substance was too unstable to permit the isolation of a pure sample for analysis, and the question whether it is the sulphoxide-sulphate or the thio-oxonium salt must for the present remain undecided, although probably a mixture is present. It is interesting to notice that the nitrate of the sulphoxide persistently retains a red tint, even when prepared from the thoroughly purified base, and it is obvious to suggest in comparison with the *o*-sulphoxides of diphenylamine (Barnett and Smiles, *loc. cit.*), of diphenylmethane (Hilditch and Smiles, Trans., 1911, **99**, 145), and of diphenyl sulphide (Fries and Vogt, *loc. cit.*) that the sulphoxide salts tend spontaneously to yield the isomeric sulphonium salts:



$$C_{10}H_6{<}\overset{OH\ \ \ Ac}{\genfrac{}{}{0pt}{}{S}{O}}{>}C_{10}H_6 \longrightarrow C_{10}H_6{\leqslant}\underset{Ac}{\overset{OH}{\genfrac{}{}{0pt}{}{S}{O}}}{>}C_{10}H_6.$$

Experiments to obtain further evidence of this are now being made.

Chloronaphthathioxin, $C_{10}H_6{<}\genfrac{}{}{0pt}{}{S}{O}{>}C_{10}H_5Cl$.

Ten grams of β-naphthasulphonium-quinone were treated for two and a-half hours with boiling acetyl chloride (100 grams). The solid rapidly dissolved, and after a short time the brown liquid deposited a voluminous mass of yellow crystals. When the reacting mixture had cooled, the solid was collected, and finally freed from adherent acetyl chloride by admixture with alcohol. The yield of the crude product was 10 grams. The substance was recrystallised from glacial acetic acid, from which it separated in feathery, lemon-yellow crystals; these melted at 173—174°:

0·1012 gave 0·2664 CO_2 and 0·0313 H_2O. C = 71·79; H = 3·44.
0·2302 „ 0·0985 AgCl. Cl = 10·59.
$C_{20}H_{11}OClS$ requires C = 71·75; H = 3·29; Cl = 10·61 per cent.

This chloro-derivative is also slowly formed by boiling a solution of the quinone in acetic acid with hydrochloric acid.

Chloronaphthathioxin Oxide, $C_{10}H_6{<}\genfrac{}{}{0pt}{}{SO}{\text{-}O\text{-}}{>}C_{10}H_5Cl$.

This substance was prepared from chloronaphthathioxin by interaction with nitric acid, the method being the same as that described with naphthathioxin oxide. The yield was almost theoretical, and when the substance had been recrystallised from glacial acetic acid it was obtained in yellow prisms, which had the appearance of sand. These melted and decomposed at 199—200°:

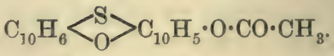
0·1009 gave 0·2541 CO_2 and 0·0282 H_2O. C = 68·68; H = 3·1.
$C_{20}H_{11}O_2ClS$ requires C = 68·47; H = 3·14 per cent.

On adding sulphuric acid to a solution of this substance in acetic acid a salt is obtained in green needles, which closely resemble those furnished by naphthathioxin oxide under similar conditions.

Dichloronaphthathioxin, $C_{10}H_5Cl{<}\genfrac{}{}{0pt}{}{S}{O}{>}C_{10}H_5Cl$.

Chloronaphthathioxin oxide was dissolved in glacial acetic acid, and an excess of concentrated hydrochloric acid was added to the hot solution. A green colour was immediately produced, but this rapidly gave place to a copious precipitate of the desired substance. The interaction was completed by heating the reacting mixture at 100° for two hours, after which the dichloronaphthathioxin was collected. The yield was almost theoretical. The substance is sparingly soluble in boiling glacial acetic acid, and readily so in hot tetrachloroethane, from which it separates in yellow needles melting at 234—235°:

0·1013 gave 0·2417 CO_2 and 0·0261 H_2O. C=65·0; H=2·8.
0·1378 „ 0·1054 AgCl. Cl=18·9.
$C_{20}H_{10}OCl_2S$ requires C=65·0; H=2·7; Cl=19·2 per cent.



Acetoxynaphthathioxin, $C_{10}H_6<{}^{S}_{O}>C_{10}H_5\cdot O\cdot CO\cdot CH_3$.

Acetic anhydride was saturated at 70—80° with 5 grams of β-naphthasulphonium-quinone, and to the solution 1 gram of camphor-β-sulphonic acid was added. The temperature was maintained at 80° for fifteen minutes, and the mixture then set aside to cool. Four grams of acetoxynaphthathioxin were precipitated in yellow leaflets, which, after being recrystallised from hot glacial acetic acid, melted at 199—200°:

0·1188 gave 0·3209 CO_2 and 0·0435 H_2O. C=73·6; H=4·0.
0·1509 „ 0·1011 $BaSO_4$. S=9·2.
$C_{22}H_{14}O_3S$ requires C=73·7; H=3·9; S=8·9 per cent.

This substance is hydrolysed by prolonged boiling with aqueous alkali hydroxide, or dilute sulphuric acid, or by brief solution in cold concentrated sulphuric acid. In either case the hydroxy-derivative is formed, but this could not be isolated in the pure condition, owing to the ease with which it is converted, apparently by oxidation, into a reddish-brown, resinous material. The same substance is formed by prolonged interaction of a cold solution of the quinone in acetic acid with a few drops of concentrated sulphuric acid. With the latter-named acid the acetoxy-derivative develops a bluish-green colour, which is characteristic of this series. Nitric acid (D 1·4) both oxidises and nitrates the substance.

Interaction of β-Naphthasulphonium-quinone and Sodium Ethoxide.

Previous experiments made with the interaction of this quinone and aqueous-alcoholic sodium hydroxide have shown (Trans., 1911, **99**, 932) that very small quantities of naphthathioxin are then formed. Others have now been made in the attempt to improve the yield of this substance, and for this purpose alcoholic sodium ethoxide was used. With this reagent the yield of naphthathioxin is still smaller, for not more than a trace is formed, the main interaction being one of reduction.

When β-naphthasulphonium-quinone was warmed with a concentrated alcoholic solution of sodium ethoxide, it rapidly dissolved, forming a yellow solution, from which a crystalline sodium salt was deposited on cooling. The reacting mixture was poured into water, and the small quantity of insoluble material was removed by filtration. The filtrate was acidified, and the precipitated material was collected and recrystallised from hot alcohol. The product was identified as β-naphthol sulphide (m. p. 212°) by its chemical behaviour and by its melting point taken alone or mixed with a sample of that substance.

In concluding this paper an account may be given of some experiments made while endeavouring to obtain other quinones of the sulphonium type.

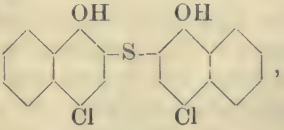
4-*Chloro*-1-*naphthol* 2-*Sulphide*, $(OH\cdot C_{10}H_5Cl)_2S$.

A solution of sulphur dichloride (SCl_2) in chloroform was added to a very thin paste of finely divided 4-chloro-α-naphthol with that solvent, the mixture being well cooled with ice-water. One molecular proportion of sulphur chloride was employed for every two such proportions of chloronaphthol taken. Immediate interaction ensued, hydrogen chloride being evolved, and the chloronaphthol passing into solution. In a few moments separation of the required substance began, and when this was complete the crystalline material was collected and washed with a little chloroform. In this manner 6 grams of the crude product were obtained from 7 grams of chloronaphthol. The substance was purified by crystallisation from hot alcohol, when it was obtained in colourless needles, which melted and decomposed at 172°:

0·1041 gave 0·2354 CO_2 and 0·0294 H_2O. C = 61·67; H = 3·1.

$C_{20}H_{12}O_2Cl_2S$ requires C = 62·0; H = 3·1 per cent.

From the general phenomena observed in the substitution of α-naphthol there can be no doubt that this sulphide has the following structure:



whence it is seen that, in comparison with the α-sulphide of β-naphthol, the position of the thio- and hydroxyl groups are inter-changed. It is remarkable that, whereas the latter sulphide is quite stable in presence of air in alkaline solution, the sulphide now described is readily oxidised under these conditions, and it thus shows a closer resemblance to the amino-naphthols which easily yield the imino-quinone under such treatment (Liebermann, *Annalen*, 1882, **211**, 55). The sulphide of 4-chloro-1-naphthol readily dissolves in aqueous alkali hydroxide, giving a yellow solution, but in presence of air a bluish-green precipitate of a sodium salt is rapidly formed. We have not been able conclusively to determine whether this substance is of quinonoid nature or not, for the blue material obtained by treating this sodium salt with mineral acids could not be obtained in the crystalline state, and is very unstable. The sulphide is also very readily oxidised in ethereal solution by ferric chloride, yielding a yellow, crystalline material. This probably contains the quinonoid structure, for it reacts with phenylhydrazine; but no further investigation was made, since analysis showed that indefinite loss of chlorine takes place during the oxidation, and the mixture of substances could not be separated.

We desire to thank the Weston Chemical Co. for kindly supplying us with the tetrachloroethane used in these experiments.

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LXXVI.—*Asymmetric Quaternary Arsonium Compounds and their Attempted Resolution.*

By THOMAS FIELD WINMILL.

THE fact that optical activity can be exhibited by substances containing no asymmetric atom other than one of quinquevalent nitrogen was first demonstrated by Pope and Peachey (Trans., 1899, **75**, 1127), who prepared *d*- and *l*-phenylbenzylmethylallylammonium iodide and bromide; since that time a considerable number of other optically active substances, containing asymmetric nitrogen atoms, have been prepared by methods similar to those used by these workers. All attempts to prepare substituted ammonium salts of which the optical activity is associated with the presence of asymmetric quinquevalent atoms of other elements of group V of the periodic classification have, however, uniformly failed (Pope and Gibson, this vol., p. 735); as these attempts have in general been made for the purpose of obtaining optically active substituted phosphonium salts, it seemed desirable to ascertain whether quaternary arsonium compounds containing an asymmetric quinquevalent arsenic atom could be obtained in optically active form.

The work on this subject described in the present paper, although unsuccessful in that it did not result in the association of optical activity with the presence of an asymmetric quinquevalent arsenic atom, led to the discovery of a number of novel reactions connected with the arsines, and is therefore now put forward.

It was confidently anticipated that on converting phenylbenzylmethylallylarsonium iodide into the corresponding *d*-camphor-β-sulphonate or *d*-α-bromocamphor-π-sulphonate, and inoculating the supersaturated solution with crystals of *d*- or *l*-phenylbenzylmethylallylammonium *d*-camphor-β-sulphonate or *d*-α-bromocamphor-π-sulphonate, resolution would be effected; it was supposed that the arsonium and ammonium salts would prove isomorphous, and that the resolution would be assisted by the great facility with which the substituted ammonium camphorsulphonates crystallise. This anticipation was not realised, and in consequence it became of interest to study further the differences in behaviour thus indicated between arsenic and nitrogen compounds of corresponding compositions and constitutions.

The following points of difference have been found to exist. When phenyltrimethylammonium iodide is heated to 360°, it ultimately yields mesidine hydriodide; after heating phenyltrimethylarsonium iodide at 400° in a sealed tube for ten hours it may be recovered unchanged, despite the fact that this substance melts and decomposes at 248° in an open tube. The arsonium compound thus dissociates into phenyldimethylarsine and methyl iodide at 400°. When phenyltrimethylammonium hydroxide is heated it yields dimethylaniline and methyl alcohol; similarly, on distilling phenyltrimethylarsonium hydroxide in a current of steam, phenyldimethylarsine passes over. At the same time a minute quantity of a solid hygroscopic substance, non-volatile with steam and too small in amount for analysis, remains dissolved in the residual liquor. Phenyldimethylamine combines readily with diazonium salts, yielding azo-compounds; phenyldimethylarsine gives deeply coloured solutions with diazonium salts, but the reaction proceeds so slowly that the diazonium solution decomposes before sufficient of the azo-compound for examination is produced. With diazotised anthranilic acid, phenyldimethylarsine gives a red-coloured solution, which acts as an indicator in the same way as methyl-red, dimethylaminoazobenzene-*o*-carboxylic acid. When an amine containing a halogen atom attached to the nitrogen atom is heated, the halogen atom enters the aromatic nucleus; phenylmethylbromoarsine, on the contrary, distils without change at 250°, and, even when heated with hydrogen bromide in acetic acid solution, affords no evidence of the migration of bromine into the nucleus.

After working for a short time with the substances now dealt with, unpleasant pathological effects are experienced. The vapours are apparently absorbed by the skin of the hands and face, and considerable nervous irritation is set up; ultimately, large blisters, resembling burns, are produced, and these disappear only after some weeks.

A considerable quantity of *phenylethyl-*n*-propylarsine*,

$$C_6H_5(C_2H_5)As{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3,$$

was prepared by the aid of the series of reactions represented by the following equations:

(1) $(C_6H_5)_3As + 2AsCl_3 = 3C_6H_5AsCl_2$.
(2) $C_6H_5{\cdot}AsCl_2 + Zn(C_2H_5)_2 = C_6H_5{\cdot}As(C_2H_5)_2 + ZnCl_2$.
(3) $C_6H_5{\cdot}As(C_2H_5)_2 + Br_2 = C_6H_5{\cdot}As(C_2H_5)_2Br_2$.
(4) $C_6H_5{\cdot}As(C_2H_5)_2Br_2 = C_6H_5(C_2H_5)AsBr + C_2H_5Br$.
(5) $2C_6H_5(C_2H_5)AsBr + Zn(C_3H_7)_2 = C_6H_5(C_2H_5)As{\cdot}C_3H_7 + ZnBr_2$.

Of these reactions, numbers (1) and (2) were described by Michaelis, La Costa, and Reise (*Annalen*, 1880, **201**, 212; *Ber.*, 1882, **15**, 2876); in connexion therewith it may be remarked that light petroleum, boiling at 40—50°, may with advantage be substituted for ether, as used by Michaelis, and that in reaction (1) a much better yield of phenylarsine dichloride may be obtained by heating at 290—300° than at 250°.

Phenyldiethylarsine dibromide, $C_6H_5(C_2H_5)_2AsBr_2$, is obtained as a precipitated, white, crystalline mass on treating a light petroleum solution of bromine with a slight excess of phenyldiethylarsine; it melts and decomposes at 85°. The decomposition proceeds rapidly at 120°, torrents of ethyl bromide being evolved and phenylethylbromoarsine being produced:

0·2880 gave 0·2931 AgBr. Br = 43·3.

$C_{10}H_{15}Br_2As$ requires Br = 43·3 per cent.

Phenylethylbromoarsine, $C_6H_5{\cdot}As(C_2H_5)Br$, is obtained in a state of purity by heating phenyldiethylarsine dibromide at 200° in a current of carbon dioxide; it forms a nearly colourless liquid, which decomposes, forming a black tar, when distilled under atmospheric pressure:

0·8036 gave 0·5642 AgBr. Br = 30·0.

$C_8H_{10}BrAs$ requires Br = 30·6 per cent.

Phenylethylchloroarsine, $C_6H_5{\cdot}As(C_2H_5)Cl$, is obtained by heating phenyldiethylarsine dichloride at 160—180° in an open flask for twenty minutes. It is a colourless, highly refractive liquid, which boils with some decomposition at 249°:

0·6622 gave 0·4302 AgCl. Cl=16·1.

$C_8H_{10}ClAs$ requires Cl=16·4 per cent.

Owing to the difficulty of regulating the amount of chlorine required in the formation of phenyldiethylarsine dichloride, it is not easy to obtain this substance in a pure state.

Phenyldiethylarsine di-iodide, $C_6H_5(C_2H_5)_2AsI_2$, prepared by treating a petroleum solution of iodine with the requisite amount of phenyldiethylarsine, is a yellow, microcrystalline substance; it melts at 95°, and decomposes at 105°:

0·5525 gave 0·5460 AgI. I=54·5.

$C_{10}H_{15}I_2As$ requires I=54·7 per cent.

*Phenylethyl-*n*-propylarsine*, $C_6H_5(C_2H_5)As \cdot C_3H_7$, is prepared by the action of zinc propyl on phenylethylbromoarsine in ethereal solution in accordance with reaction (5); it is a colourless liquid, which boils at 245° without decomposition, and possesses the characteristic arsine odour. The tertiary arsine behaves as a very feeble base, and is not soluble in concentrated hydrochloric acid; it appears to oxidise but very slowly on exposure to the air.

*Phenylbenzylmethyl-*n*-propylarsonium iodide*,

$$C_6H_5(C_7H_7)(CH_3)(C_3H_7)AsI,$$

is formed on heating a mixture of phenylethyl-*n*-propylarsine and benzyl iodide in molecular proportion at 40—50°; the reaction is complete in about two hours. The residue crystallises readily from ethyl acetate, and the salt is then obtained in small, colourless crystals, melting at 128°; the substance is readily soluble in alcohol, but insoluble in water:

0·5530 gave 0·2943 AgI. I=28·77.

$C_{18}H_{24}IAs$ requires I=28·75 per cent.

*Phenylbenzylethyl-*n*-propylarsonium* d*-camphor-β-sulphonate*,

$$C_6H_5 \cdot CH_2(C_6H_5)(C_2H_5)(C_3H_7)As \cdot SO_3 \cdot C_{10}H_{15}O,$$

is prepared by treating the foregoing compound in alcoholic solution with the requisite amount of silver *d*-camphor-β-sulphonate; after warming for some time reaction is complete, and the filtrate from the silver iodide yields, on evaporation, a viscous mass, which crystallises after some days. The salt is readily soluble in most organic solvents and in water, and is purified by fractional crystallisation from a mixture of acetone and light petroleum:

0·2179 gave 0·4907 CO_2 and 0·1501 H_2O. C=61·4; H=7·15.

$C_{28}H_{39}O_4SAs$ requires C=61·5; H=7·2 per cent.

No evidence of resolution was obtained during the fractional crystallisation of the salt, and the following determinations of rotatory power indicate that in aqueous solution the substance exhibits practically the molecular rotatory power of the acid ion:

0·5036 gram, made up to 30 c.c. with water at 15°, gave $\alpha + 0{\cdot}81^\circ$ in a 4-dcm. tube; $[\alpha]_{\text{Hg green}} + 11{\cdot}9^\circ$ and $[M]_{\text{Hg green}} + 64{\cdot}9^\circ$.

On mixing concentrated aqueous solutions of the salt and potassium iodide, the corresponding iodide is precipitated and proved to be completely inactive in alcoholic solution.

Phenylethyl-n-*propylallylarsonium bromide*,

$$C_6H_5(C_3H_5)(C_2H_5)(C_3H_7)AsBr,$$

is prepared by the interaction of phenylethyl-*n*-propylarsine and allyl bromide; combination is complete in about twenty-four hours, and a solid, crystalline mass is obtained. The salt crystallises from acetone in large, colourless plates, melting at 86°, and is moderately soluble in water. The corresponding d-*α-bromocamphor-π-sulphonate*, $C_6H_5(C_3H_5)(C_2H_5)(C_3H_7)As\cdot SO_3\cdot C_{10}H_{14}OBr$, crystallises readily from dilute alcohol; it melts at 123°:

0·2051 gave 0·3446 CO_2 and 0·1130 H_2O. C = 50·4; H = 6·13.
$C_{24}H_{36}BrI_4SAs$ requires C = 50·1; H = 6·26 per cent.

The following determination of rotatory power was made with salt which had been recrystallised six times from acetone, and indicates that no resolution had been effected; the molecular rotatory power is practically that of the bromocamphorsulphonic acid ion in aqueous solution:

0·6252 gram, made up to 30 c.c. with water at 15°, gave $\alpha_{\text{Hg green}} + 5{\cdot}00^\circ$; $[\alpha]_{\text{Hg green}} + 60^\circ$ and $[M]_{\text{Hg green}} + 345^\circ$.

Preparation of Phenylmethylallylarsine.

Since phenylbenzylmethylallylammonium iodide appears to be the most easily resolved of the known asymmetric quaternary ammonium compounds, it was decided, in view of the failure to resolve the arsonium salts above described, to attempt the preparation of the arsenic analogue of this ammonium derivative. For this purpose either phenylmethylallylarsine or phenylbenzylmethylarsine was required, and, as neither of these substances can be prepared by means of reactions (1) to (5), special methods of preparation had to be devised. As the result of a great deal of preliminary work, phenylmethylallylarsine was obtained by aid of the following series of reactions:

(6) $C_6H_5{\cdot}AsCl_2 + 2CH_3{\cdot}MgI = C_6H_5{\cdot}As(CH_3)_2 + MgClI$.
(7) $C_6H_5{\cdot}As(CH_3)_2 + Br_2 = C_6H_5{\cdot}As(CH_3)_2Br_2$.
(8) $C_6H_5{\cdot}As(CH_3)_2Br_2 = C_6H_5{\cdot}As(CH_3)Br + CH_3Br$.
(9) $C_6H_5{\cdot}As(CH_3)Br + C_3H_5I + Mg = C_6H_5{\cdot}As(CH_3){\cdot}C_3H_5 + MgBrI$.

Phenyldimethylarsine was prepared by Michaelis and Link (*Annalen*, 1881, **207**, 205) by the action of zinc methyl on phenylarsenic dichloride; this method, however, gives a poor yield, mainly because of the difficulty of obtaining zinc methyl free from methyl iodide, the presence of which results in the formation of a quaternary arsonium compound. A much better yield (40 per cent. of theory) is obtained by the action of phenylarsenic dichloride diluted with ether on magnesium methyl iodide; the yield may be increased to 75 per cent. of the theoretical by diluting the phenylarsenic dichloride with light petroleum, boiling at 30—40°, instead of with ether. After treatment with water the phenyldimethylarsine is separated in the usual manner as a colourless oil, having the properties assigned to it by Michaelis and Link. On very cautiously treating its 5 per cent. solution in light petroleum with a 5 per cent. solution of bromine in the same solvent, and filtering off the petroleum, *phenyldimethylarsine dibromide*, $C_6H_5{\cdot}As(CH_3)_2Br_2$, remains as a white, crystalline, slightly hydroscopic solid, which melts at 128° with violent decomposition. If, in this preparation, the phenyldimethylarsine is not constantly in excess, *phenyldimethylarsine tetrabromide*, $C_6H_5{\cdot}As(CH_3)_2Br_4$, is produced. The latter compound, which is one of a class not previously described, is conveniently made by adding bromine (20 grams) to a light petroleum solution of phenyldimethylarsine (5 grams); a dark red oil separates, which crystallises on repeated washing with light petroleum. It forms dark red crystals, which melt at 61° without decomposition, and which, when heated at 160° for fifteen minutes, leave a residue of pure phenylarsenic dibromide; each molecule of the tetrabromide thus decomposes quantitatively, yielding one molecule of phenylarsenic dibromide and two molecules of methyl bromide. Analysis of the latter product indicated the presence of 50·7 per cent. of bromine, whilst the pure dibromide requires 51·2 per cent.:

0·5798 required 46·4 c.c. $N/10$-$AgNO_3$. Br = 64·0.

$C_8H_{11}Br_4As$ requires Br = 63·75 per cent.

On heating phenyldimethylarsine dibromide at 180° until effervescence ceases and purifying the oily residue by repeated distillation, *phenylmethylbromoarsine*, $C_6H_5{\cdot}As(CH_3)Br$, is obtained as a colourless liquid boiling at 250° without decomposition:

0·5492 gave 0·6067 AgBr. Br = 47·0.

C_7H_8BrAs requires Br = 46·8 per cent.

The displacement of the bromine atom in phenylmethylbromoarsine by either the allyl or the benzyl radicle proved to be difficult; magnesium benzyl bromide acts on the bromoarsine, with formation of a mixture of products which could not be separated. Mercuric allyl iodide reacts violently with phenylmethylbromoarsine, yielding a gummy mass, which is not acted on by boiling dilute potassium hydroxide or by dilute acids.

Although allyl iodide in ethereal solution yields diallyl when treated with magnesium dust, it was found that the latter acts vigorously on a mixture of phenylmethylbromoarsine and allyl iodide in molecular proportion and in presence of ether, with the formation of very little diallyl; on working up the product in the usual way a liquid arsine of high boiling point was obtained. After repeated fractionation through a column in a current of hydrogen, impure *phenylmethylallylarsine*, $C_6H_5\cdot As(CH_3)\cdot C_3H_5$, was obtained as a colourless liquid boiling at 192°; further purification was impracticable, because slight decomposition occurs on distillation and because the arsine is too feebly basic to form stable salts.

On allowing a mixture of the impure arsine to remain for several days after mixing with the calculated quantity of benzyl iodide, a vitreous hygroscopic mass results, which can be caused to crystallise from acetone solution. After repeated crystallisation from this solvent, and finally from a mixture of acetone and alcohol, *phenylbenzylmethylallylarsonium iodide*,

$$C_6H_5\cdot CH_2(C_6H_5)(C_3H_5)(CH_3)AsI,$$

is obtained in large, colourless crystals, melting at 100°. A very poor yield was obtained. The substance is insoluble in water, but dissolves readily in acetone, alcohol, or ethyl acetate:

0·3272 gave 0·1814 AgI. I=29·96.

$C_{17}H_{23}IAs$ requires I=29·81 per cent.

The above iodide reacts readily with the calculated quantity of silver *d*-*α*-bromocamphor-*π*-sulphonate under the usual conditions, and the resulting solution yields *phenylbenzylmethylallylarsonium* d-*α-bromocamphor-π-sulphonate*,

$$C_6H_5\cdot CH_2(C_6H_5)(C_3H_5)(CH_3)As\cdot SO_3\cdot C_{10}H_{14}OBr,$$

as a crystalline residue on evaporation. The salt crystallises from a mixture of alcohol and acetone in large, colourless prisms, melting at 189°:

0·2007 gave 0·3922 CO_2 and 0·1020 H_2O. C=53·4; H=5·6.

$C_{27}H_{34}O_4BrSAs$ requires C=53·2; H=5·6 per cent.

The following determination of rotatory power was made with salt which had been recrystallised four times from a mixture of alcohol and acetone:

0·5378 gram, made up to 30 c.c. with water at 15°, gave $\alpha_{\mathrm{Hg\ green}} + 4{\cdot}22°$ in a 4-dcm. tube, whence $[\alpha]_{\mathrm{Hg\ green}} + 58{\cdot}8°$ and $[M]_{\mathrm{Hg\ green}} + 357°$.

The value of $[M]_{\mathrm{Hg\ green}}$ for the *d*-bromocamphorsulphonic ion is +347° (Pope and Read, Trans., 1910, **97**, 2201), appreciably less than that just given; repeated crystallisation of the salt led to no change in the rotation constants, and it must consequently be concluded that no resolution had been effected. Further, the iodides precipitated from the solutions of the salt by addition of potassium iodide were all optically inactive. No separation could be caused by inoculating concentrated solutions with crystals of *d*- or *l*-phenylbenzylmethylallylammonium *d*-α-bromocamphor-π-sulphonate.

The salt of the asymmetric arsonium base with *d*-camphor-β-sulphonic acid was also prepared, but this could not be caused to crystallise, even by inoculating the syrupy solution with crystals of *d*- and *l*-phenylbenzylmethylallylammonium *d*-camphor-β-sulphonate.

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LXXVII.—*The Four Stereoisomeric Optically Active 2 : 4-Dimethyltetrahydroquinolines.*

By John Thomas.

The dialkyltetrahydroquinolines, in which the two alkyl radicles are attached to separate carbon atoms in the piperidine ring, contain two asymmetric carbon atoms in the molecule, and would hence be expected to exist in two pairs of enantiomorphously related optically active isomerides; the reduction product of a dialkylquinoline containing the two alkyl radicles in the pyridine ring should thus yield a mixture of four optically active substances. In general, the dialkyltetrahydroquinolines prepared by reducing the corresponding dialkylquinolines have been described as single substances, and it seemed therefore of interest to ascertain whether in any particular case the four isomerides referred to could be actually separated from the synthetic secondary base.

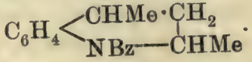
The investigation of 2 : 4-dimethyltetrahydroquinoline was undertaken for the purpose of resolving the problem indicated, and it is shown in the present paper that the synthetic base may be resolved into four optically active components; the separation was effected by crystallisation of the base with *d*- and *l*-*α*-bromocamphor-*π*-sulphonic acids, as first employed by Pope and Harvey (Trans., 1901, **79**, 74). The synthetic 2:4-dimethyltetrahydroquinoline may thus be regarded as composed of two externally compensated bases, which may be conveniently distinguished as the 2:4-dimethyltetrahydroquinoline and the *iso*-2:4-dimethyltetrahydroquinoline; the distinction thus introduced is, of course, an arbitrary one.

2:4-*Dimethyl- and* iso-2:4-*Dimethyl-tetrahydroquinoline.*

2:4-Dimethylquinoline is formed, as described by Beyer (*J. pr. Chem.*, 1886, [ii], **33**, 401), by the interaction of paraldehyde, acetone, and aniline; several hundred grams were prepared and purified by means of the picrate, the base boiling at 263—266° being used for reduction. It was found that 2:4-dimethylquinoline is not reduced by tin and hydrochloric acid, as are the monomethylquinolines, but as Ferratini (*Gazzetta*, 1893, **23**, ii, 117) states that the base can be reduced by sodium and alcohol, without giving details, the following method of reduction was employed with success.

2:4-Dimethylquinoline (50 grams) is dissolved in absolute alcohol (500 grams) in a large flask, and sodium (75 grams) added in small portions; during the latter stages of the reaction the flask is heated to 150° on an oil-bath for about two hours. After solution of the sodium, water and hydrochloric acid are added, the alcohol distilled off, and excess of potassium hydroxide added; the separated base is extracted with benzene, and the benzene extract fractionally distilled after drying with potassium hydroxide. 2:4-Dimethyltetrahydroquinoline (45 grams) is thus obtained as a colourless oil boiling at 250—254°.

Benzoyl-2:4-*dimethyltetrahydroquinoline*,



$$C_6H_4<\begin{array}{l}CHMe\cdot CH_2\\ \qquad\qquad\;\; | \\ NBz\text{---}CHMe\end{array}.$$

The benzoyl derivative, prepared by the Schotten-Baumann reaction, crystallises from dilute alcohol in thin, colourless plates, melting at 115—116°; it is very soluble in alcohol or benzene, but less so in acetone, chloroform, or ethyl acetate:

0·2450 gave 0·7325 CO_2 and 0·1595 H_2O. C=81·5; H=7·23.

$C_{18}H_{19}ON$ requires C=81·5; H=7·17 per cent.

As the fractional crystallisation of the benzoyl derivative gave no immediate indication of a separation, the resolution of the mixed base with the optically active acid was attempted.

d-2:4-*Dimethyltetrahydroquinoline* d-*α-Bromocamphor-π-sulphonate*, $C_{11}H_{15}N,C_{10}H_{14}OBr\cdot SO_3H$.

2 : 4-Dimethyltetrahydroquinoline and *d*-α-bromocamphor-π-sulphonic acid, in molecular proportion, were boiled together in dilute alcoholic solution until all had dissolved; a viscid oil separated on cooling, and this gradually crystallised during several days in the vacuum desiccator. The semicrystalline mass was pressed on the filter and freed from oil by repeated crystallisation from hot dilute alcohol; after seven crystallisations the specific rotatory power in dilute aqueous solution attained the constant value of $[\alpha]_D$ +84·4°. The salt crystallises in voluminous, white needles, and melts at 126°, previously softening at 119°. It is extremely soluble in alcohol, readily so in acetic acid, benzene, chloroform, or acetone, and only moderately so in water or ethyl acetate:

0·2008 gave 0·3906 CO_2 and 0·1154 H_2O. C=53·1; H=6·33.

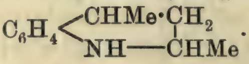
$C_{21}H_{30}O_4NBrS$ requires C=53·4; H=6·35 per cent.

As the rotation constants vary considerably with the solvent in the cases of this and other substances described in the present paper, a considerable number of determinations were made, all at 18°.

Solvent.	Weight in grams in 25 c.c.	α_D in 2-dcm. tube.	$[\alpha]_D$.	$[M]_D$.
Water	0·1040	+0·72°	+86·2°	+407°
	0·2052	1·395	84·9	401
	0·3090	2·10	85·0	401
	0·4100	2·84	86·5	408
Benzene	0·1500	0·82	68·3	322
	0·3000	1·62	67·8	320
Chloroform	0·1570	1·05	83·6	395
	0·2940	1·99	84·6	399
Acetone	0·1488	1·08	90·7	428
	0·2980	2·15	90·2	426
Ethyl alcohol...............	0·1600	1·27	99·2	468
	0·3385	2·67	98·7	466
Ethyl acetate,..............	0·1595	1·23	96·4	456
	0·3145	2·45	97·3	459
Acetic acid..................	0·1367	1·18	107·6	508
	0·2582	2·73	105·8	500

Disregarding the first determination in aqueous solution as not possessed of much accuracy owing to the dilution of the solution, the molecular rotatory power of the salt in dilute aqueous solution may be taken as $[M]_D$ +401°; allowing the value $[M]_D$ +279° for the acidic ion (Pope and Read, Trans., 1910, **97**, 2201), the molecular rotatory power of the basic ion is calculated as $[M]_D$ +122°. It is shown below that the molecular rotatory power of the basic ion, as calculated from observations made with the hydrochloride, is greater than $[M]_D$ +160°; another instance is thus added to those recorded by Pope and Read (this vol., p. 775) of the abnormal molecular rotatory powers of salts of the type *dBdA* in aqueous solution.

d-2:4-*Dimethyltetrahydroquinoline*,



$$C_6H_4<\begin{matrix}CHMe\cdot CH_2\\ \qquad\quad | \\ NH—CHMe\end{matrix}.$$

On distilling the salt just described with barium hydroxide in a current of steam, extracting the oil from the distillate with benzene, drying the benzene solution with potassium hydroxide, and subjecting it to fractional distillation, d-2:4-*dimethyltetrahydroquinoline* is obtained as a colourless oil boiling at 251—254°. The base is miscible with organic solvents, is practically insoluble in water, and gradually darkens in colour on exposure to the air; on cooling in boiling liquid air it solidifies to a hard, resinous mass. The following determinations of rotatory power were made:

The observed rotation in a 2·4-dcm. tube at 20° is $\alpha + 14{\cdot}49°$, and the density at 20°/4° is 1·0009, whence $[\alpha]_D + 60{\cdot}13°$ and $[M]_D + 97{\cdot}1°$.

0·2945 gram, made up to 20 c.c. with alcohol at 18°, gave $\alpha_D + 1{\cdot}68°$ in a 2-dcm. tube, whence $[\alpha]_D + 57{\cdot}0°$ and $[M]_D + 91{\cdot}8°$.

0·7350 gram, made up to 20 c.c. with alcohol at 18°, gave $\alpha_D + 3{\cdot}31°$ in a 2-dcm. tube, whence $[\alpha]_D + 56{\cdot}7°$ and $[M]_D + 91{\cdot}3°$.

d-2:4-*Dimethyltetrahydroquinoline Hydrochloride*, $C_{11}H_{15}N,HCl$.

The hydrochloride separates in radiate groups of long, colourless prisms on cooling a hot solution of the base in concentrated hydrochloric acid; after washing with hydrochloric acid and crystallisation from hot water, the salt melts at 226°. It is readily soluble in warm alcohol, sparingly so in acetone, and practically insoluble in benzene or chloroform:

0·1510 gave 0·3680 CO_2 and 0·1117 H_2O. C = 66·5; H = 8·21.

$C_{11}H_{15}N,HCl$ requires C = 66·8; H = 8·10 per cent.

The following determinations of the rotation constants were made:

0·1155 gram, made up to 25 c.c. with water at 18°, gave $\alpha_D + 0{\cdot}79°$ in a 2-dcm. tube, whence $[\alpha]_D + 84{\cdot}4°$ and $[M]_D + 167°$.

0·2270 gram, made up to 25 c.c. with water at 18°, gave $\alpha_D + 1{\cdot}51°$ in a 2-dcm. tube, whence $[\alpha]_D + 83{\cdot}1°$ and $[M]_D + 164{\cdot}5°$.

0·1072 gram, made up to 25·4 c.c. with alcohol at 19°, gave α_D +0·775° in a 2-dcm. tube, whence $[\alpha]_D$ +91·4° and $[M]_D$ +181°.

Benzoyl-d-2 : 4-*dimethyltetrahydroquinoline.*

The benzoyl derivative is prepared by the action of benzoyl chloride and sodium hydroxide on the bromocamphorsulphonate, and, after crystallisation from dilute alcohol, is obtained in colourless, crystalline plates, which melt at 98—99°; it is readily soluble in benzene or alcohol, moderately so in acetone, ethyl acetate, or acetic acid, and very sparingly soluble in light petroleum:

0·2003 gave 0·5790 CO_2 and 0·1305 H_2O. C=81·2; H=7·15.

$C_{18}H_{19}ON$ requires C=81·5; H=7·17 per cent.

The rotation constants were determined at 18° as follows:

Solvent.	Weight in grams in 25 c.c.	α_D in 2-dcm. tube.	$[\alpha]_D$.	$[M]_D$.
Benzene	0·1696	−4·24°	−312·5°	−828°
	0·3028	7·60	313·7	831
Ethyl alcohol	0·1254	3·81	379·7	1006
	0·2811	8·52	378·9	1004
Acetone.....................	0·1045	3·13	374·5	992
	0·2905	8·76	377·0	999
Chloroform	0·1064	3·18	373·6	990
	0·2056	6·22	378·1	1002
Ethyl acetate	0·0980	3·12	397·7	1054
	0·1919	6·03	392·8	1041
Acetic acid	0·1237	4·14	418·2	1109
	0·2118 (in 25·9 c.c.)	6·88	420·6	1114

The introduction of the benzoyl radicle has converted the dextrobase into a highly lævorotatory substance; the same kind of change of sign of the rotation constants is observed on benzoylating tetrahydroquinaldine (Pope and Peachey, Trans., 1899, **75**, 1066), tetrahydro-*p*-toluquinaldine (Pope and Rich, Trans., 1899, **75**, 1093), and bornylamine (Forster, Trans., 1898, **73**, 386).

l-iso-2 : 4-*Dimethyltetrahydroquinoline* d-α-*Bromocamphor*-π-*sulphonate*, $C_{11}H_{15}N,C_{10}H_{14}OBr{\cdot}SO_3H$.

On concentrating the mother liquors remaining after the separation of *d*-2 : 4-dimethyltetrahydroquinoline *d*-α-bromocamphor-π-sulphonate, an oily residue is obtained, which slowly becomes partly crystalline; the crystalline material is separated as far as possible from the residual oil, and fractionally crystallised from very dilute alcohol. The two salts just named above are then obtained in crystalline form; *l-iso*dimethyltetrahydroquinoline *d*-α-bromocamphor-π-sulphonate is distinguished from the isomeride in that it forms small, colourless, cube-shaped crystals, melting at 176—178°, and is more soluble in dilute alcohol:

0·2045 gave 0·3990 CO_2 and 0·1182 H_2O. C=53·2; H=6·38.
$C_{21}H_{30}O_4NBrS$ requires C=53·4; H=6·35 per cent.

It is difficult to purify this salt, and only a small quantity was obtained in a pure condition; the following determination of rotatory power was made on a specimen of which the rotation constants remained unchanged by further crystallisation:

0·2585 gram, made up to 25 c.c. with water at 18°, gave α_D +1·44° in a 2-dcm. tube, whence $[\alpha]_D$ +55·7° and $[M]_D$ +263°.

These values agree fairly with those obtained with the enantiomorphously related salt, which, as is shown below, is more easily prepared.

l-iso-2:4-*Dimethyltetrahydroquinoline*, $C_{11}H_{15}N$.

On distillation with barium hydroxide in a current of steam, the above salt yields *l*-iso-2:4-dimethyltetrahydroquinoline, which is purified in the same way as the isomeride previously described; the base is a nearly colourless oil boiling at 243—244°, and slowly darkens in the air. The following determinations of rotatory power were made:

The base exhibits the rotatory power of α_D −4·35° in a 2·4-dcm tube at 15°, and its density at 15°/4° is 1·0063, whence $[\alpha]_D$ −18·03° and $[M]_D$ −29·05°.

0·1903 gram, made up to 20 c.c. at 18° with alcohol, gave α_D −0·335° in a 2-dcm. tube, whence $[\alpha]_D$ −17·6° and $[M]_D$ −28·2°.

0·6371 gram, made up to 25 c.c. with alcohol at 18°, gave α_D −0·91° in a 2-dcm. tube, whence $[\alpha]_D$ −17·9° and $[M]_D$ −28·8°.

l-iso-2:4-*Dimethyltetrahydroquinoline Hydrochloride*, $C_{11}H_{15}N,HCl$.

This salt and the other optically active hydrochlorides now described are conveniently prepared by dissolving the base in a little concentrated hydrochloric acid, dissolving the product in alcohol, and gradually adding ether; under this treatment *l-iso*-2:4-dimethyltetrahydroquinoline yields the hydrochloride as a crystalline, white powder, melting at 178—180°:

0·1135 gave 0·2774 CO_2 and 0·0825 H_2O. C = 66·6; H = 8·09.

$C_{11}H_{15}N,HCl$ requires C = 66·8; H = 8·10 per cent.

The following determination of rotatory power was made:

0·3010 gram, made up to 20 c.c. with water at 18°, gave α_D −0·18°, whence $[\alpha]_D$ −5·1° and $[M]_D$ −10·1°.

On heating the solution for two hours on the water-bath it darkened in colour, but did not change in rotatory power.

Benzoyl-l-iso-2 : 4-*dimethyltetrahydroquinoline*, $C_{11}H_{14}N{\cdot}CO{\cdot}C_6H_5$.

The benzoyl derivative is obtained in theoretical yield by the Schotten-Baumann reaction, and is purified by recrystallisation from alcohol; it forms small, colourless, cube-shaped crystals, melting at 90°. The compound is very soluble in alcohol, ethyl acetate, acetone, or benzene, and sparingly so in light petroleum:

0·2210 gave 0·6540 CO_2 and 0·1465 H_2O. C = 80·8; H = 7·32.

$C_{18}H_{19}ON$ requires C = 81·5; H = 7·17 per cent.

The examination of a number of alcoholic solutions of the substance showed it to be optically inactive in alcohol; this behaviour is not, however, due to optical inversion, because on hydrolysis by boiling with concentrated hydrochloric acid the optically active base was recovered.

l-2 : 4-*Dimethyltetrahydroquinoline* l-*α-Bromocamphor-π-sulphonate.*

After the separation of as large a proportion as possible of the two optically active bases above described, the mixture of bases contained in the mother liquors is separated with barium hydroxide in the usual manner; a strongly lævorotatory base, exhibiting the value α_D −12° to −13° in a 1-dcm. tube, results, and this is then dissolved in boiling dilute alcohol, with the addition of the corresponding quantity of *l*-*α*-bromocamphor-*π*-sulphonic acid. On cooling, an oil separates, which can only be caused to crystallise with great difficulty and after long keeping; the crystalline deposit is fractionally crystallised from alcohol, as in the case of the previously described salts, and is thus resolved into two pure substances, which prove to be enantiomorphously related to the *d*-bromocamphorsulphonates dealt with above. *l*-2 : 4-Dimethyltetrahydroquinoline *l*-*α*-bromocamphor-*π*-sulphonate resembles its enantiomorphously related isomeride in general properties; its rotation constants were determined as follows:

Solvent.	Weight in grams in 25 c.c.	$\alpha_{\rm D}$ in 2-dcm. tube at 18°.	$[\alpha]_{\rm D}$.	$[M]_{\rm D}$.
Water	0·1125	−0·77°	−85·5°	−404°
	0·2135	1·48	86·1	407
	0·3825 (in 20 c.c.)	3·27	84·7	400
Benzene	0·1042	0·57	68·4	323
	0·2180	1·19	68·2	322
Chloroform	0·1055	0·695	82·4	389
	0·2154	1·43	82·9	391
Ethyl alcohol...............	0·1165	0·915	98·1	462
	0·2118	1·65	97·5	460
Acetic acid	0·1145	0·982	107·1	505
	0·2328	1·96	105·2	496
Ethyl acetate...............	0·2510	1·95	97·2	459
	0·1148 (in 20 c.c.)	1·09	95·8	452
Acetone	0·1525	0·92	91·1	430

Good agreement exists between these values and those obtained for the enantiomorphously related salt.

l-2 : 4-*Dimethyltetrahydroquinoline.*

This base closely resembles its *d*-isomeride, and exhibits the following rotation constants:

The rotation $\alpha_{\rm D}$ −13·75° was observed in a 2·4-dcm. tube at 20°, and the density was determined at 20°/4° as 1·00078, whence $[\alpha]_{\rm D}$ −57·24° and $[M]_{\rm D}$ −92·15°.

0·2540 gram, made up to 20 c.c. with alcohol, gave $\alpha_{\rm D}$ −1·43° in a 2-dcm. tube at 18°, whence $[\alpha]_{\rm D}$ −56·2° and $[M]_{\rm D}$ −90·6°.

0·5250 gram, made up to 20 c.c. with alcohol, gave $\alpha_{\rm D}$ −2·94° in a 2-dcm. tube at 18°, whence $[\alpha]_{\rm D}$ −56·0° and $[M]_{\rm D}$ −90·2°.

These values are a little lower than those obtained with the enantiomorphously related compound.

l-2 : 4-*Dimethyltetrahydroquinoline Hydrochloride.*

This salt forms a white, crystalline powder melting at 226°, and was obtained in larger quantity in a pure condition than was its isomeride, because the parent base formed the major proportion of the mixture from which it was separated. The following determinations of rotatory power thus possess considerable accuracy:

Solvent.	Weight in grams in 20 c.c.	$\alpha_{\rm D}$ in 2-dcm. tube.	$[\alpha]_{\rm D}$.	$[M]_{\rm D}$.
Water	0·1165	−0·95°	−81·5°	−161·2°
	0·2245 (in 25·2 c.c.)	1·44	80·8	159·8
Alcohol	0·1082	0·99	91·4	180·5
	0·2920	2·18	93·2	184·5

Benzoyl-l-2 : 4-*dimethyltetrahydroquinoline.*

The benzoyl derivative crystallises in plates melting at 98—99°, and is highly dextrorotatory:

0·1895 gave 0·5578 CO_2 and 0·1224 H_2O. C = 80·7; H = 7·20.

$C_{18}H_{19}ON$ requires C = 81·5; H = 7·17 per cent.

The values obtained for the rotation constants agree closely with those given above for the enantiomorphously related isomeride.

Solvent.	Weight in grams.	Volume in c.c.	Temperature.	α_D in 2-dcm. tube.	$[\alpha]_D$.	$[M]_D$.
Benzene	0·1214	25·0	19°	+3·05°	+314·1°	+832·3°
	0·0790	20·0	18	2·485	314·7	833·7
	0·2023	25·0	18	5·08	313·5	830·3
Ethyl alcohol ...	0·0715	20·0	18	2·71	377·6	1000·6
Acetic acid.........	0·0890	25·0	19	2·99	420·0	1113·0
Ethyl acetate ...	0·0455	20·2	19	1·81	401·7	1063·0

The externally compensated 2:4-dimethyltetrahydroquinoline obtained by mixing equal quantities of the two components does not crystallise on cooling in boiling liquid air; the corresponding *hydrochloride* forms a white, crystalline powder, melting at 220—222°. A mixture of the two optically active benzoyl derivatives in equal proportion yields the externally compensated benzoyl derivative described above.

d-iso-2:4-*Dimethyltetrahydroquinoline* l-α-*Bromocamphor-π-sulphonate.*

The preparation of this salt has been already described above; the substance forms small, cube-shaped crystals, melting at 176—178°:

0·2175 gave 0·4240 CO_2 and 0·1246 H_2O. C = 53·2; H = 6·38.

$C_{21}H_{30}O_4NBrS$ requires C = 53·4; H = 6·33 per cent.

The molecular rotatory power of the basic ion was determined by the following polarimetric measurements made in water solution at 18°; the weights of substance given were made up to 25 c.c.:

Weight in grams.	α_D in 2-dcm. tube.	$[\alpha]_D$.	$[M]_D$.
0·3215	−1·42°	−55·2°	−261°
0·3353	1·47	54·8	259
0·2215	0·975	55·4	262
0·1140	0·51	55·5	262

d-iso-2:4-*Dimethyltetrahydroquinoline.*

This base was obtained as a pale yellow oil, which boils at 244—246°. In a 2·4-dcm. tube at 15° it exhibited the rotatory power α_D +4·40°, and the density, determined at 15°/4°, was found to be 1·0044, whence $[\alpha]_D$ +18·23° and $[M]_D$ +29·52°.

0·5254 gram, made up to 25 c.c. with alcohol at 18°, gave α_D +0·975° in a 2-dcm. tube, whence $[\alpha]_D$ +18·5° and $[M]_D$ +29·7°.

0·6920 gram, made up to 25 c.c. with alcohol at 17°, gave α_D +1·025° in a 2-dcm. tube, whence $[\alpha]_D$ +18·5° and $[M]_D$ +29·7°.

These values show a close agreement with those given for the enantiomorphously related base.

d-iso-2:4-*Dimethyltetrahydroquinoline Hydrochloride.*

This salt forms a colourless, crystalline powder, melting at 178—180°; during its purification, and also in that of the enantiomorphously related isomeride, some evidence was obtained of the presence of an externally compensated hydrochloride, so that it is possible that the separation of the two *iso*-bases by means of the corresponding bromocamphorsulphonates is not quite perfect:

0·1505 gave 0·3677 CO_2 and 0·1100 H_2O. C = 66·3; H = 6·15.

$C_{11}H_{15}N,HCl$ requires C = 66·8; H = 8·10 per cent.

0·2170 gram, made up to 20 c.c. with water at 18°, gave α_D + 0·68° in a 2-dcm. tube, whence $[\alpha]_D$ + 5·1° and $[M]_D$ + 10·1°.

A mixture of *d*- and *l*-iso-2:4-dimethyltetrahydroquinoline in equal proportions boiled at 246°, and did not crystallise when cooled in boiling liquid air.

In order to ascertain the proportion in which the two externally compensated bases are present in the reduction product of 2:4-dimethylquinoline, 48 grams of the tetrahydrodimethylquinoline were dissolved in dilute alcohol with the requisite amount of *d*-bromocamphorsulphonic acid, and the resolution effected as described above; each crystalline product was carefully fractionated, and its rotatory power determined. Whilst 141 grams of the mixture of four salts should have been obtained, the following quantities were actually separated in a fair state of purity:

23·6 grams of *d*-base, *d*-acid giving $[\alpha]_D$ + 86·2° in water.
23·0 ,, of *l*-base, *l*-acid giving $[\alpha]_D$ − 86·5° in water.
21·1 ,, of *l-iso*-base, *d*-acid giving $[\alpha]_D$ + 55·4° in water.
21·6 ,, of *d-iso*-base, *l*-acid giving $[\alpha]_D$ − 54·8° in water.

The total quantity of salt separated was thus 89 grams in place of the 141 grams originally present; the balance of the material was oily, and could not be extracted in the form of pure salts. So far as these results can be interpreted, it would appear that the two externally compensated bases are produced in approximately equal quantities during the reduction of 2:4-dimethylquinoline.

The author desires to express his thanks to Professor Pope for suggesting and supervising the work now described.

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LXXVIII.—*Some Mixed Phosphonium Derivatives.*

By William Jackson Pope and Charles Stanley Gibson.

During several years past we have been occupied in attempts to prepare optically active phosphonium compounds containing no asymmetric atom other than one of quinquevalent phosphorus. Although these attempts have hitherto proved unsuccessful, a number of results of interest have been arrived at which it seems desirable to record.

Preparation of Phosphenyl Chloride.

The method of preparing phosphenyl chloride devised by Michaelis (*Annalen*, 1876, **181**, 283), which consists in slowly distilling a mixture of equal volumes of benzene and phosphorus trichloride through a red-hot porcelain tube, is a satisfactory one. An essential improvement on the original method consists, however, in keeping a slow stream of carbon dioxide continually passing through the apparatus; the yield of pure phosphenyl chloride is then considerably greater than that obtained by Michaelis, and one litre of the mixture affords about 140 grams of the pure product per nine hours. The fractional distillation of the product is conveniently carried out in a stream of carbon dioxide, and the phosphenyl chloride preserved in glass-stoppered bottles filled with carbon dioxide.

Mercury Dibenzyl, $Hg(CH_2{\cdot}C_6H_5)_2$.

Magnesium powder (12 grams) and benzyl chloride (87 grams) are caused to react in ether solution under the conditions described by Kipping (Trans., 1907, **91**, 720); finely powdered mercuric chloride (52 grams) is then added in small portions with constant agitation. The mixture is finally heated on the water-bath for two hours, and, after cooling, treated successively with water and dilute hydrochloric acid. The mercury dibenzyl is extracted with benzene, the benzene extract evaporated, and the residue crystallised from boiling benzene after washing with ether:

0·4024 gave, by the Carius method, 0·2452 HgS. Hg = 52·51.

$C_{14}H_{14}Hg$ requires Hg = 52·34 per cent.

Mercury dibenzyl crystallises from benzene in thin, lustrous, doubly-refracting plates, melting at 104°. It is readily soluble in carbon disulphide or chloroform, moderately so in benzene or ethyl acetate, and very sparingly so in cold alcohol. It is practically insoluble in ether or light petroleum; it is insoluble in water, and is not decomposed on boiling with that solvent. The substance possesses a characteristic, sweet odour, which becomes nauseating when large quantities of the material are dealt with.

A similar method to the above was used by Pfeiffer and Truskier (*Ber.*, 1904, **37**, 1125) for the preparation of mercury diphenyl, and it was anticipated that by heating mercury dibenzyl with phosphenyl chloride it would be possible to prepare phenylbenzylchlorophosphine in accordance with a well-known reaction stated by Michaelis. This reaction does not proceed, however, in this case, because mercury dibenzyl decomposes into mercury and dibenzyl at about 170°, whilst reactions of the type referred to do not set in until a much higher temperature has been attained. Similarly, it was not found possible to isolate the secondary chlorophosphine from the product of reaction of phosphenyl chloride with magnesium benzyl chloride; even on treating phosphenyl chloride with magnesium methyl iodide the only product which could be isolated in any quantity was an oil which when treated with methyl iodide gave phenyltrimethylphosphonium iodide. The latter was identified by analysis, and crystallises from alcohol in long, colourless prisms, melting at 226—227°, instead of at 205°, as stated by Michaelis (*loc. cit.*, p. 363).

p-*Tolylmercuric Bromide.*

In view of the failure to cause interaction between phosphenyl chloride and mercury dibenzyl, it was decided to introduce the *p*-tolyl group into the phosphorus compound by the aid of a mercury compound; on treating magnesium *p*-tolyl bromide with mercuric chloride, the previously unknown *p*-tolylmercuric bromide was obtained.

p-Bromotoluene (120 grams) was slowly added to magnesium dust (12 grams) suspended in ether, reaction being allowed to proceed with but little rise of temperature; mercuric chloride (52 grams) was then added in portions, and the solution heated on the water-bath for four to six hours. After distillation of the ether, dilute hydrochloric acid was added, the solid product collected, and freed from di-*p*-tolyl and *p*-bromotoluene by extraction with alcohol and chloroform. The residue was obtained in thin scales of a pearl-grey lustre, melting at 228°, by crystallisation from boiling benzene:

0·5610 gave 0·2751 AgBr. Br = 20·87.

C_7H_7HgBr requires Br = 21·54 per cent.

The p-*tolylmercuric bromide* thus obtained (48 grams) represents a 70 per cent. yield; it is sparingly soluble in the ordinary solvents when hot, and practically insoluble in the cold.

Phenyl-p-*tolylchlorophosphine.*

On heating phosphenyl chloride (78 grams) with *p*-tolylmercuric bromide (60 grams) for two to three hours at 270° in a flask provided with a reflux condenser, through which a stream of dry carbon dioxide passes, vigorous reaction occurs; on cooling, the product is extracted with benzene, and the benzene solution fractionally distilled after filtering. Phosphenyl chloride (24 grams) is recovered, and a 63·5 per cent. yield of phenyl-*p*-tolylchlorophosphine (30 grams), boiling at 230—240°/100 mm., was obtained; the latter product was further identified with the compound obtained by Michaelis by conversion into phenyl-*p*-tolylphosphinic acid, and by comparison with the substance prepared as described by this author (*Annalen*, 1896, **293**, 263).

It is obvious that the reaction between mercury di-*p*-tolyl and phosphenyl chloride proceeds in accordance with the following equation:

$$2(C_6H_5)PCl_2 + (C_6H_4Me)_2Hg = 2C_6H_4Me(C_6H_5)PCl + HgCl_2,$$

and not in accordance with that given by Michaelis.

Phenyl-p-*tolylmethylallylphosphonium Iodide*, $C_6H_5(C_6H_4Me)(C_3H_5)(CH_3)PI$.

Phenyl-*p*-tolylmethylphosphine (22 grams), prepared by the action of phenyl-*p*-tolylchlorophosphine on zinc methyl as described by Michaelis, was treated with allyl iodide (20 grams) in dry ether solution; after remaining for a short time in a freezing mixture, a crystalline deposit was formed, and this, when action was at an end, was crystallised from alcohol containing a little water, and finally from a mixture of alcohol and ether. The substance forms colourless, glistening needles, which begin to decompose at 170° and melt at 175—177°; it is soluble in water or alcohol, less so in acetone, and insoluble in ether, benzene, or light petroleum:

0·2108, titrated with $AgNO_3$ and NH_4CNS, indicated 0·0698 I. I = 33·14.

$C_{17}H_{20}IP$ requires I = 33·22 per cent.

On treating this iodide with equivalent quantities of the silver salts of *d*-camphor-β-sulphonic acid, *d*-α-bromocamphor-π-sulphonic acid, and *d*-α-bromocamphor-β-sulphonic acid respectively in aqueous solution and evaporating the filtrate, viscid residues were obtained, which could not be caused to crystallise.

The iodide is decomposed with effervescence by treating with silver hydroxide in presence of water, and the corresponding phosphonium hydroxide could not be obtained.

Phenyl-p-*tolylbenzylmethylphosphonium Bromide*, $C_6H_5(C_6H_4Me)(C_6H_5{\cdot}CH_2)(CH_3)PBr$.

This substance crystallised rapidly from a mixture of equivalent quantities of phenyl-*p*-tolylmethylphosphine and benzyl bromide cooled in a freezing mixture, and was purified by recrystallisation from a mixture of acetone and ether. It forms thin, colourless plates, melting at 211—212°, is easily soluble in acetone, and insoluble in ether or benzene:

0·1972, with $AgNO_3$ and NH_4CNS, showed 0·0408 Br. Br = 20·67.

$C_{21}H_{22}BrP$ requires Br = 20·70 per cent.

dl-*Phenyl*-p-*tolylbenzylmethylphosphonium* d-*α-Bromocamphor-π-sulphonate*, $C_6H_5(C_6H_4Me)(C_6H_5{\cdot}CH_2)(CH_3)P{\cdot}O{\cdot}SO_2{\cdot}C_{10}H_{14}OBr$.

On treating the phosphonium bromide with the corresponding amount of the silver salt of the optically active acid in hot alcoholic solution, filtering and evaporating the filtrate, a gum remains which crystallises on being kept in a desiccator. The salt is purified by several crystallisations from boiling benzene, and then forms colourless needles, which on rapid heating sinter at 122° and melt at 129—131°:

0·5752 lost 0·0174 at 105° in three hours. $H_2O = 3·02$.

0·1070 * gave 0·2364 CO_2 and 0·0626 H_2O. C = 60·25; H = 6·49.

$C_{31}H_{36}O_4BrSP,1H_2O$ requires $H_2O = 2·84$ per cent.

$C_{31}H_{36}O_4BrSP$ requires C = 60·49; H = 5·90 per cent.

On subjecting the salt to systematic fractional crystallisation from a mixture of ethyl acetate and acetone, it was resolved into three fractions, which exhibited the specific rotatory powers for mercury green light of [α] + 53·9°, + 53·4°, and + 53·9° respectively in 1 per cent. aqueous solutions. It is thus indicated that the phosphonium base is not resolved into optically active components by crystallisation with the optically active acid employed.

The rotation constants of the salt were determined in aqueous solution, using a carefully purified sample; 0·2658 gram in 30 c.c., examined in a 4-dcm. tube at 15°, gave the following values:

	$\text{Mercury}_{\text{green}}$.	$\text{Mercury}_{\text{yellow}}$.	$\text{Sodium}_{\text{yellow}}$.
α............	+ 1·91°	+ 1·625°	+ 1·555°
[α].........	53·9	45·85	43·74
[M].........	331	282	269

The rotatory dispersions are for $\text{Hg}_{\text{green}}/\text{Na}_{\text{yellow}} = 1·232$ and for $\text{Hg}_{\text{yellow}}/\text{Na}_{\text{yellow}} = 1·048$.

For purposes of comparison, careful determinations were made of the rotation constants of ammonium *d*-α-bromocamphor-π-sulphonate in an aqueous solution of equivalent concentration; 0·1464 gram of the ammonium salt, made up to 30 c.c. and examined in a 4-dcm. tube at 15°, gave the following values:

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* Anhydrous.

	Mercury$_{\text{green}}$.	Mercury$_{\text{yellow}}$.	Sodium$_{\text{yellow}}$.
α	+ 2·03°	+ 1·715°	+ 1·64°
[α]	104·0	87·9	84·0
[M]	341	288	276

The rotatory dispersions are for $Hg_{\text{green}}/Na_{\text{yellow}} = 1·238$ and for $Hg_{\text{yellow}}/Na_{\text{yellow}} - 1·046$.

The several fractions of the salt were treated in aqueous solution with potassium iodide, and the crystalline iodide which was precipitated was found to be optically inactive in methyl-alcoholic solution. It is thus proved that the asymmetric phosphonium compound has not been resolved into optically active components by crystallisation of its *d*-*α*-bromocamphor-*π*-sulphonate.

dl-*Phenyl*-p-*tolylbenzylmethylphosphonium* d-*Camphor*-*β*-*sulphonate*.

The above salt was prepared in a similar manner to the preceding one, and crystallises readily from ethyl acetate containing a little alcohol in colourless needles melting at 134—137°. It is readily soluble in alcohol or acetone, but sparingly so in ethyl acetate:

0·1101 gave 0·2792 CO_2 and 0·0732 H_2O. C = 69·15; H = 7·39.

$C_{31}H_{37}O_4SP$ requires C = 69·33; H = 6·95 per cent.

After careful fractional crystallisation from ethyl acetate and alcohol, the several fractions proved to have the same specific rotatory power, and the following determinations establish the constants for the salt; 0·3175 gram, made up to 30 c.c. with water, gave the following values in a 4-dcm. tube at 15°:

	Mercury$_{\text{green}}$.	Mercury$_{\text{yellow}}$.	Sodium$_{\text{yellow}}$.
α	+ 0·52°	+ 0·42°	+ 0·39°
[α]	12·3	9·9	9·2
[M]	66	53	49

The rotatory dispersions are for $Hg_{\text{green}}/Na_{\text{yellow}} = 1·333$ and for $Hg_{\text{yellow}}/Na_{\text{yellow}} = 1·075$.

The following determinations of the rotation constants of ammonium *d*-camphor-*β*-sulphonate in aqueous solution of equivalent concentration serve for comparison; 0·1494 gram was made up to 30 c.c. with water and examined in a 4-dcm. tube at 15°:

	Mercury$_{\text{green}}$.	Mercury$_{\text{yellow}}$.	Sodium$_{\text{yellow}}$.
α	+ 0·53°	+ 0·43°	+ 0·40°
[α]	26·6	21·6	20·1
[M]	66	54	50

The rotatory dispersions are for $Hg_{\text{green}}/Na_{\text{yellow}} = 1·325$ and for $Hg_{\text{yellow}}/Na_{\text{yellow}} = 1·075$.

On addition of potassium iodide to the aqueous solutions of the several fractions, the corresponding phosphonium iodide is precipitated, and each sample thus obtained proved optically inactive in methyl-alcoholic solution. It is thus indicated that the resolution of the asymmetric phosphonium salt into optically active components has not been effected.

Phenyl-p-*tolylbenzylmethylphosphonium Iodide*, $C_6H_5(C_6H_4Me)(C_6H_5\cdot CH_2)(CH_3)PI$.

This substance is obtained by the addition of potassium iodide to the aqueous solution of any of its above soluble salts; on crystallisation from alcohol it is obtained in colourless, glistening plates, melting at 215—216·5°. It dissolves readily in methyl alcohol, less so in hot alcohol, and is practically insoluble in ether, benzene, or light petroleum:

0·3538, with $AgNO_3$ and NH_4CNS, indicated 0·1030 I. I=29·11.

$C_{21}H_{22}IP$ requires I=29·38 per cent.

Phenyl-p-*tolylbenzylmethylphosphonium Platinichloride*, $[C_6H_5(C_6H_4Me)(C_6H_5\cdot CH_2)(CH_3)P]_2PtCl_6$.

This salt is precipitated as a yellow, crystalline powder on addition of chloroplatinic acid to the aqueous solution of either of its above soluble salts; it is practically insoluble in all the ordinary solvents, and melts at 214—215°:

0·1131 gave 0·2040 CO_2 and 0·0491 H_2O. C=49·14; H=4·82.

$(C_{21}H_{22}P)_2PtCl_6$ requires C=49·52; H=4·35 per cent.

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LXXIX.—*The Alkaloidal Salts of Phenylmethylphosphinic Acid.*

By WILLIAM JACKSON POPE and CHARLES STANLEY GIBSON.

MEISENHEIMER and Lichtenstadt (*Ber.*, 1911, **44**, 356) have recently succeeded in resolving phenylmethylethylphosphine oxide,

$CH_3(C_2H_5)(C_6H_5)PO$,

into optically active components by Pope and Peachey's method (Trans., 1898, **73**, 893); Kipping and his pupils (Trans., 1909, **95**, 1993; 1911, **99**, 626) have also obtained strong evidence indicating that asymmetric organic derivatives of phosphoric acid are also resolvable by crystallisation with optically active bases. It appeared therefore desirable to attempt the resolution of some asymmetric derivative of phosphinic acid, and for this reason we have endeavoured to separate phenylmethylphosphinic acid,

$$CH_3(C_6H_5)P{:}O(OH),$$

into optically active components by crystallisation with optically active alkaloids. We have been unable to effect such a resolution, and, inasmuch as we have prepared a number of well crystallised salts of the acid with optically active bases, a considerable amount of evidence, negative in character, is now available, indicating that phenylmethylphosphinic acid is not resolvable into optically active components. The only suggestion which we can at present offer in explanation of this is the possibility that the acid in question may be readily converted into the ortho-form, $CH_3(C_6H_5)P(OH)_3$, even when present as a salt.

Phenylmethylphosphinic Acid.

This acid was prepared by a slight modification of the process given by Michaelis (*Annalen*, 1896, **293**, 220), which consists in heating phenyldipiperidylmethylphosphonium hydroxide at 150° for three to four hours, and evaporating the residue with ammonia on the water-bath until the solution is free from ammonia; after filtration the silver salt is obtained as a voluminous, white precipitate by addition of silver nitrate, and, after filtration, is accurately precipitated with hydrochloric acid. The filtrate from the silver chloride yields the free acid on evaporation on the water-bath; a 75 per cent. yield of pure, crystalline phenylmethylphosphinic acid, melting at 133—134°, is thus obtained.

l-*Menthylamine Phenylmethylphosphinate*,

$$CH_3(C_6H_5)PO_2H,C_{10}H_{19}\cdot NH_2.$$

This salt was obtained as a white, powdery mass on evaporating a benzene solution of corresponding quantities of *l*-menthylamine and phenylmethylphosphinic acid to dryness; after crystallisation from a mixture of dry acetone and ethyl acetate, the salt was separated into six fractions by crystallisation from ethyl acetate containing a little alcohol. The fractions form long, colourless, feathery needles, melting at 188—189°, are very soluble in water or alcohol, much less so in ethyl acetate, and sparingly soluble in acetone:

0·1046 gave 0·2516 CO_2 and 0·0934 H_2O. C = 65·60; H = 9·99.

$C_{17}H_{30}O_2NP$ requires C = 65·52; H = 9·71 per cent.

That no resolution has been effected is shown by comparison of the rotation constants of the first and last of the six fractions.

Fraction 1.

0·2376 Gram, made up to 30 c.c. with water at 15°. $l=4$ dcm.

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α	− 0·83°	− 0·73°	− 0·71°
$[\alpha]$	26·2	23·0	22·4
[M]	81·6	71·7	69·8

Rotatory dispersions: $Hg_{green}/Na_{yellow}=1·169$; $Hg_{yellow}/Na_{yellow}=1·028$.

Fraction 6.

0·2486 Gram, made up to 30 c.c. with water at 15°. $l=4$ dcm.

α	− 0·87°	− 0·76°	− 0·74°
$[\alpha]$	26·2	22·9	22·3
[M]	81·7	71·4	69·5

Rotatory dispersions: $Hg_{green}/Na_{yellow}=1·176$; $Hg_{yellow}/Na_{yellow}=1·027$.

Confirmation of the conclusion that no resolution had been effected was obtained by determining the rotation constants in aqueous solutions of equivalent concentrations of the *l*-menthylamine hydrochloride used; the values obtained were $[\alpha]_D$ −36·4° and $[M]_D$ −69·7°. The latter value is experimentally identical with the corresponding values obtained for the two fractions of salt.

Cinchonine Phenylmethylphosphinate,
$CH_3(C_6H_5)PO_2H,C_{19}H_{22}ON_2,2H_2O$.

On evaporating equivalent quantities of the acid and the alkaloid in alcoholic solution on the water-bath, the above salt rapidly crystallises; after eliminating excess of either component by crystallisation from ethyl acetate the salt was resolved into fractions by twenty-six crystallisations from this solvent. The extreme fractions were then again crystallised from water, and thus obtained in small, colourless needles; both fractions appeared identical, but the melting points were not sharp. This was traced to the presence of water of crystallisation, and the highest melting point observed was 170—172°. The salt is very soluble in alcohol or hot benzene, and sparingly so in ethyl acetate:

0·1253 gave 0·2952 CO_2 and 0·0850 H_2O. C = 64·09; H = 7·54.

0·4718 lost 0·0342 at 103—110°. H_2O = 7·25.

$C_{26}H_{31}O_3N_2P,2H_2O$ requires C = 64·31; H = 7·26;
H_2O = 7·40 per cent.

The following rotatory-power determinations of the first and last fractions were made:

First Fraction.

0·2630 Gram, made up to 30 c.c. with water at 17°. $l=4$ dcm.

	$\mathrm{Hg}_{\text{green}}$.	$\mathrm{Hg}_{\text{yellow}}$.	$\mathrm{Na}_{\text{yellow}}$.
α	+ 5·30°	+ 4·63°	+ 4·45°
$[\alpha]$	151·0	132·0	126 9
[M]	735	642	617

Rotatory dispersions : $\mathrm{Hg}_{\text{green}}/\mathrm{Na}_{\text{yellow}}=1{\cdot}191$; $\mathrm{Hg}_{\text{yellow}}/\mathrm{Na}_{\text{yellow}}=1{\cdot}040$.

Last Fraction.

0·2610 Gram, made up to 30 c.c. with water at 17°.

α	+ 5·24°	+ 4·58°	+ 4·40°
$[\alpha]$	150·5	131·5	126·5
[M]	732	640	615

Rotatory dispersions : $\mathrm{Hg}_{\text{green}}/\mathrm{Na}_{\text{yellow}}=1{\cdot}190$; $\mathrm{Hg}_{\text{yellow}}/\mathrm{Na}_{\text{yellow}}=1{\cdot}040$.

It is clear that no resolution has been effected, and the molecular rotatory powers given may be taken as those of the cinchonine ion.

Cinchonidine Phenylmethylphosphinate,
$CH_3(C_6H_5)PO_2H,C_{19}H_{22}O_2N,4H_2O$.

This salt was obtained as a crystalline residue on evaporating an alcoholic solution of its components on the water-bath. After systematic fractionation by twenty recrystallisations from ethyl acetate and from water, no resolution appeared to have occurred. The salt crystallises from water in beautiful, colourless prisms, melting at 154°; it is very soluble in alcohol, benzene, or boiling water, and sparingly so in ethyl acetate or cold water:

0·1212 gave 0·2672 CO_2 and 0·0900 H_2O. C = 60·12; H = 8·31.
0·5443 lost 0·0736 at 110°. H_2O = 13·52.
$C_{26}H_{31}O_3N_2P,4H_2O$ requires C = 59·87; H = 8·49;
H_2O = 13·79 per cent.

The rotatory powers of the extreme fractions were determined in alcoholic solution at 17·5°.

First Fraction.

0 2650 Grams in 30 c.c. $l=4$ dcm.

	$\mathrm{Hg}_{\text{green}}$.	$\mathrm{Hg}_{\text{yellow}}$.	$\mathrm{Na}_{\text{yellow}}$.
α	− 3·01°	− 2·60°	− 2·49°
$[\alpha]$	85·1	73·6	70·5
[M]	444	384	368

Rotatory dispersions : $\mathrm{Hg}_{\text{green}}/\mathrm{Na}_{\text{yellow}}=1{\cdot}207$; $\mathrm{Hg}_{\text{yellow}}/\mathrm{Na}_{\text{yellow}}=1{\cdot}044$.

Last Fraction.

0·2746 Gram in 30 c.c. $l=4$ dcm.

α	− 3·12°	− 2·69°	− 2·58°
[α]	85·4	73·5	70·5
[M]	446	384	368

Rotatory dispersions: $\text{Hg}_{\text{green}}/\text{Na}_{\text{yellow}}=1{\cdot}211$; $\text{Hg}_{\text{yellow}}/\text{Na}_{\text{yellow}}=1{\cdot}043$.

Quinine Phenylmethylphosphinate,
$CH_3(C_6H_5)PO_2H,C_{20}H_{24}O_2N_2,4H_2O$.

On evaporating an alcoholic solution of corresponding quantities of the alkaloid and acid to dryness, this salt remains as a bulky, white, crystalline powder; when crystallised from ethyl acetate containing a little alcohol, the salt was obtained in fractions which differed in melting point and in rotatory power, but these differences were ultimately traced to the absorption of atmospheric moisture by the various fractions. On prolonged fractional crystallisation from water the material was separated into a number of fractions which proved to be identical; the hydrated salt commences to melt at 85°, but the anhydrous salt melts at 164—166°. It is readily soluble in alcohol or in hot ethyl acetate and water, but dissolves sparingly in cold water:

0·1042 gave 0·2238 CO_2 and 0·0720 H_2O. C = 58·57; H = 7·73.
0·5392 lost 0·0714 at 110°. H_2O = 13·24.
$C_{27}H_{33}O_4N_2P,4H_2O$ requires C = 58·65; H = 7·48;
H_2O = 13·05 per cent.

The following determinations of the rotation constants of extreme fractions were made in alcoholic solutions at 15° in 4-dcm. tubes:

First Fraction.

0·2032 Gram in 30 c.c.

	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.
α	− 3·83°	− 3·28°	− 3·07°
[α]	141·4	121·1	113·3
[M]	781	669	625

Rotatory dispersions: $\text{Hg}_{\text{green}}/\text{Na}_{\text{yellow}}=1{\cdot}248$; $\text{Hg}_{\text{yellow}}/\text{Na}_{\text{yellow}}=1{\cdot}068$.

Last Fraction.

0·1980 Gram in 30 c.c.

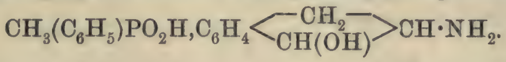
α	− 3·72°	− 3·19°	− 3·00°
[α]	140·9	120·8	113·6
[M]	778	667	627

Rotatory dispersions: $\text{Hg}_{\text{green}}/\text{Na}_{\text{yellow}}=1{\cdot}240$; $\text{Hg}_{\text{yellow}}/\text{Na}_{\text{yellow}}=1{\cdot}063$.

The practical identity of the rotation constants for the first and final fractions again indicates that no resolution has been effected.

On attempting to form a salt between phenylmethylphosphinic acid and *l*-tetrahydroquinaldine, the acid was found to crystallise unchanged from the base.

Hydroxyhydrindamine Phenylmethylphosphinate,



$CH_3(C_6H_5)PO_2H,C_6H_4<\begin{matrix}CH_2\\CH(OH)\end{matrix}>CH\cdot NH_2.$

When a solution of corresponding amounts of externally compensated hydroxyhydrindamine (Pope and Read, Trans., 1911, **99**, 2079) and the phosphinic acid in alcohol is evaporated, a crystalline salt separates, and is readily purified by crystallisation from alcohol. It forms light, silky needles, which decompose at about 170° without melting, and is readily soluble in alcohol, but dissolves sparingly in ethyl acetate or acetone:

0·1476 gave 0·3424 CO_2 and 0·0906 H_2O. C = 63·25; H = 6·87.

$C_{16}H_{20}O_3NP$ requires C = 62·91; H = 6·61 per cent.

For comparison with the above fully racemic salt, the corresponding salt of *l*-hydroxyhydrindamine was prepared.

l-*Hydroxyhydrindamine Phenylmethylphosphinate.*

This salt crystallises on evaporating an alcoholic solution of its components; it was separated into four fractions by prolonged crystallisation from ethyl acetate containing a little alcohol, and is thus obtained in long, silky needles, which begin to decompose at 175°, and subsequently melt. The salt is very soluble in alcohol or water, but almost insoluble in ethyl acetate:

0·1175 gave 0·2705 CO_2 and 0·0686 H_2O. C = 62·77; H = 6·53.

$C_{16}H_{20}O_3NP$ requires C = 62·91; H = 6·61 per cent.

The following determinations of the rotation constants were made on the extreme fractions in aqueous solutions at 17° in 4-dcm. tubes:

First Fraction.

0·2546 Gram in 30 c.c.

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α	− 0·80°	− 0·69°	− 0·67°
[α]	23·6	20·3	19·7
[M]	71·9	62·6	60·2

Rotatory dispersions: Hg_{green}/Na_{yellow} = 1·194; Hg_{yellow}/Na_{yellow} = 1·030.

Last Fraction.

0·2492 Gram in 30 c.c.

α	− 0·78°	− 0·67°	− 0·65°
$[\alpha]$	23·5	20·2	19·6
[M]	71·6	61·5	59·7

Rotatory dispersions : $\mathrm{Hg_{green}/Na_{yellow}} = 1·201$; $\mathrm{Hg_{yellow}/Na_{yellow}} = 1·031$.

It is thus obvious that the acid is not resolved by crystallisation with *l*-hydroxyhydrindamine.

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LXXX.—*The Optical Activity of Salts and Derivatives of* d-*Camphor-β-sulphonic Acid.*

By JOSEPH IVON GRAHAM (1851 Exhibition Research Scholar).

IN view of the extended use now made of the methods of resolving externally compensated bases by Pope and his pupils, it is highly desirable that accurate measurements should be made of the rotatory powers exhibited by salts and derivatives of the optically active acids concerned. The author has therefore, at the suggestion of Professor Pope, prepared and determined the rotation constants of a number of salts of *d*-camphor-β-sulphonic acid for mercury-green, mercury-yellow, and sodium lights, using water as the solvent, for the purpose of ascertaining to what extent the molecular rotatory powers are dependent on the concentration of the solution.

Amongst the salts used in the present work, some, those, namely, of zinc, calcium, barium, and ammonium, have been described by previous workers (Pope and Gibson, Trans., 1910, **97**, 2211); the author has checked their compositions by determinations of the water of crystallisation. The new salts, namely, those of magnesium, cadmium, copper, and piperidine, have been completely analysed.

The aqueous solutions of the salts were examined in 4-dcm. tubes at concentrations of 2, 4, 8, and, if solubility permitted, 16 per cent. (in the case of the ammonium salt, from 1 to 16 per cent.). All the measurements were made at 20°, duplicate series of readings being taken in every case for the same concentration.

The results obtained show that, in the case of the zinc, magnesium, and cadmium salts, no change in rotatory power for either mercury green, mercury yellow, or sodium lights, except within the limits of experimental error, takes place in solutions varying in concentration from 2 to 8 per cent. in the case of the zinc and magnesium salts, and from 2 to 16 per cent. in the case of the cadmium salt.

With solutions of the calcium and barium salts, however, increase of concentration is accompanied by slight diminution in rotatory power, the rotatory dispersion, however, remaining constant; thus for the calcium salt, $[M]^{20^\circ}_{D}$ at 2 per cent. = 98·9°; 4 per cent., 98·5°; 8 per cent., 97·1°; and 16 per cent., 95·6°. A similar change is observed in the case of the barium salt, $[M]^{20^\circ}_{D}$ varying from 98·6° at 2 per cent. to 95° at 16 per cent. concentration.

With the ammonium and piperidine salts, on the other hand, increase of concentration produces a slight but unmistakable increase in the rotatory power; thus for the former salt, $[M]^{20^\circ}_{D}$ for 1 per cent. is 50·38°; 2 per cent., 50·45°; 4 per cent., 51·0°; 8 per cent., 51·0°; and 16 per cent., 51·85°, corresponding increases being observed for the mercury green and yellow rays respectively.

Only a limited number of observations could be made with solutions of the copper salt, owing to the strong absorptive power of the solution for all light except the bluish-green; thus it was only possible to examine solutions of this salt with the mercury green ray, and owing to the general weakening of ~~the light by~~ passing through 4-dcm. thickness of solution, it was not practicable to examine a greater concentration than 4 per cent. The examination of 2, 3, and 4 per cent. solutions gave evidence of a slight diminution of $[M]^{20^\circ}_{\text{Hg green}}$ with increasing concentration.

It was found inadvisable to examine solutions of smaller concentration than 2 per cent., as the angle of rotation was then too small for the result to be of value for this investigation.

From the results thus briefly summarised it is evident that increase of concentration of the salts of *d*-camphor-β-sulphonic acid in aqueous solution produces:

(1) in the case of some salts, *no appreciable change* in rotatory power;

(2) in the case of some *a diminution* in rotatory power;

(3) in the case of other salts *an increase* in rotatory power.

It will thus appear evident that these observed changes cannot be dependent on the change of degree of electrolytic dissociation alone, but depend principally on the character of the metallic atom or electropositive grouping, since the above results show that similar effects are produced by members of the same group in the periodic classification. It also appears evident that the atomic weight of the metal in combination cannot be an important factor in this question of change of rotatory power.

EXPERIMENTAL.

d-Camphor-β-sulphonic acid was prepared by Reychler's method (*Bull. Soc. chim.*, 1898, [iii], **19**, 120). The crude acid was recrystallised several times from glacial acetic acid, and finally from ethyl acetate. This acid was kept over solid potassium hydroxide and sulphuric acid in an exhausted desiccator for several days to free the acid from traces of acetic acid.

The metallic salts were prepared from this purified acid and the carbonates of the metals, being purified by recrystallisation (at least three times), from aqueous solution.

The ammonium and piperidine salts were prepared from the acid and aqueous solutions of the base, the latter being added in slight excess, and the excess then removed by evaporation.

These two salts were purified by repeated recrystallisation—the ammonium salt from aqueous solution, but in the case of the piperidine salt purification was effected by repeated crystallisation from acetone, the salt being exceedingly soluble in water.

In the examination of the rotatory powers of the salts at different concentrations, all the solutions were made up at 20°, "conductivity" distilled water being employed as solvent.

For the same solution (that is, the same concentration) the polarimetric readings were always made in duplicate, the two series of readings in practically all cases not differing by more than 0·01°.

All the solutions were examined in 4-dcm. tubes at 20°, the temperature being kept constant by means of a brass jacket, through which water at 20° was circulated from a thermostat, the tubes being kept at 20° for at least three-quarters of an hour before examination.

Magnesium Salt, $(C_{10}H_{15}O_4S)_2Mg,6H_2O$.—This salt crystallises beautifully from water, a solution saturated at 20° containing about 10 per cent. of the hexahydrate:

0·5921 gave 0·1127 $Mg_2P_2O_7$. Mg = 4·16.
1·3356 lost 0·2422 at 195°. H_2O = 18·14.
$(C_{10}H_{15}O_4S)_2Mg,6H_2O$ requires Mg = 4·09; H_2O = 18·18 per cent.

Cadmium Salt, $(C_{10}H_{15}O_4S)_2Cd,6H_2O$.—This salt is more soluble than the magnesium one; it loses all water of crystallisation below 200°:

1·0070 gave 0·2124 CdS. Cd = 16·41.
0·5121 lost 0·0809 below 200°. H_2O = 15·80.
$(C_{10}H_{15}O_4S)_2,6H_2O$ requires Cd = 16·46; H_2O = 15·83 per cent.

Copper Salt, $(C_{10}H_{15}O_4S)_2Cu,6H_2O$:
0·9991 gave 0·1257 CuO. Cu=10·05.
1·0802 „ 0·1356 CuO. Cu=10·03.
1·1788 „ 0·1485 CuO. Cu=10·07.
$(C_{10}H_{15}O_4S)_2Cu,6H_2O$ requires Cu=10·03 per cent.
$(C_{10}H_{15}O_4S)_2Cu,5\frac{1}{2}H_2O$ „ Cu=10·18 „ „

It would therefore appear that the hexahydrate formula represents the constitution of the copper salt more nearly than $(C_{10}H_{15}O_4S)_2Cu,5\frac{1}{2}H_2O$ (Pope and Gibson, Trans., 1910, **97**, 2216). On heating to 100° for several hours, loss of weight corresponding with $4H_2O$ is produced, the salt then being of a pale blue colour.

The following determinations were made in aqueous solutions at 20° for the mercury green line:

Approximate concentration, per cent.	Grams in 29·979 c.c. at 20°.	α.	[α].	[M].
2	0·6073	1·714°	21·15°	134·1°
3	0·9025	2·528	21·00	133·15
4	1·2063	3·369	20·94	132·8

Estimations of the amount of water of crystallisation in the zinc, calcium, and barium salts were found to agree with the figures calculated from the established formulæ of these salts.

Piperidine Salt, $C_{10}H_{15}O_4S,C_5H_{12}N$.—This salt was purified by repeated crystallisation from acetone, the melting point of the pure salt being 140°. As is described more fully later on, this salt was found to be identical with the so-called piperido-lactone of *d*-camphor-β-sulphonic acid (Armstrong and Lowry, Trans., 1902, **81**, 1449; Lowry and Magson, Trans., 1906, **89**, 1050), being produced in small quantities during the preparation of the piperidide of this acid. The salt is extremely soluble in water and most organic solvents; it crystallises in stellate groups of needles from a warm solution of acetone, being much more soluble in the hot than in the cold solvent. If, however, in recrystallisation the acetone solution is evaporated too far, the resulting crystals of piperidine salt are found to melt at quite a low temperature, varying from 50° to 100°, and the salt has evidently become decomposed or altered in constitution. If these crystals are heated in a water-oven for some days, the melting point is found to have become raised again to about 134° (m. p. of pure salt=140°).

A sample of the salt, the melting point of which had become lowered to approximately 50° in the above manner, gave $[\alpha]_D^{20}$ 29·3°, whence $[M]_D^{20}$ 93·2°, in chloroform solution, whereas $[M]_D^{20}$ =102·3° for the pure piperidine salt (m. p. 140°). The two results practically agree if we assume that in the compound of low melting point two molecules of water are present; $[M]_D^{20°}$ for the latter being then 103·7°. The rotatory dispersion, Hg_{green}/Na_{yellow}, is practically the same as that for the pure piperidine salt in chloroform solution.

On heating at 110—130° for fourteen hours, 0·2527 gram of the sample melting about 50° lost 0·018, the melting point of the residue being 90—100°. It seems probable, therefore, that the piperidine salt also exists in the form of a dihydrate,

$$C_{10}H_{15}OSO_3,C_5H_{12}N,2H_2O,$$

the melting point of which lies about 50°.

Piperidine Salt, m. p. 140°:

0·1182 gave 0·2440 CO_2 and 0·0880 H_2O. C=56·30; H=8·35.
0·1484 ,, 0·3060 CO_2 ,, 0·1122 H_2O. C=56·24; H=8·47.

$C_{10}H_{15}O_4S,C_5H_{12}N$ requires C=56·71; H=8·59 per cent.,

whereas a *piperidide* or *piperido-lactone*:

$C_{10}H_{15}O_3S,C_5H_{10}N$ requires C=60·13; H=8·43 per cent.

No loss in weight was produced by heating the salt at 95—100° for seven and a-half hours.

Rotatory Powers and Rotatory Dispersions at Different Concentrations.—The following figures represent the mean values of the two series of measurements made for each concentration:

Zinc Salt, $(C_{10}H_{15}O_4S)_2Zn,6H_2O$.

Approximate concentration, per cent.	Sodium yellow.			Mercury.					
				Yellow.			Green.		
	$\alpha^{20°}$.	$[\alpha]^{20°}$.	$[M]^{20°}$.	$\alpha^{20°}$.	$[\alpha]^{20°}$.	$[M]^{20°}$.	$\alpha^{20°}$.	$[\alpha]^{20°}$.	$[M]^{20°}$.
2	1·281°	15·83°	100·7°	1·362°	16·84°	107·1°	1·678°	20·75°	131·95°
4	2·531	15·79	100·5	2·706	16·89	107·4	3·349	20·90	133·0
8	5·086	15·80	100·55	5·392	16·75	106·55	6·675	20·74	131·95

Concentrations: approximately 2 per cent.: 0·6069 gram in 30·006 c.c. at 20°.
,, 4 ,, 1·2005 ,, 29·979 ,, ,,
,, 8 ,, 2·4150 ,, 30·006 ,, ,,

Rotatory dispersions:

Approximate concentration, per cent.	Hg_{yellow}/Na_{yellow}.	Hg_{green}/Na_{yellow}.
2	1·063	1·310
4	1·069	1·323
8	1·060	1·312
Mean	1·064	1·315

Magnesium Salt, $(C_{10}H_{15}O_4S)_2Mg,6H_2O$.

Approximate concentration, per cent.	Sodium yellow.			Mercury.					
				Yellow.			Green.		
	α^{20°.	$[\alpha]^{20^\circ}$.	$[M]^{20^\circ}$.	α^{20°.	$[\alpha]^{20^\circ}$.	$[M]^{20^\circ}$.	α^{20°.	$[\alpha]^{20^\circ}$.	$[M]^{20^\circ}$.
2	1·366°	16·88°	100·4°	1·449°	17·92°	106·6°	1·797°	22·22°	132·2°
4	2·762	16·92	100·7	2·942	18·02	107·1	3·612	22·12	131·6
8	5·416	16·82	100·1	5·770	17·92	106·6	7·149	22·20	132·0

Concentrations : approximately 2 per cent. : 0·6068 gram in 30·006 c.c. at 20°.
,, 4 ,, 1·2248 ,, ,, ,,
,, 8 ,, 2·4154 ,, ,, ,,

Rotatory dispersions :

Approximate concentration, per cent.	Hg_{yellow}/Na_{yellow}.	Hg_{green}/Na_{yellow}.
2	1·061	1·316
4	1·065	1·308
8	1·065	1·320
Mean	1·064	1·315

Cadmium Salt, $(C_{10}H_{15}O_4S)_2Cd,6H_2O$.

Approximate concentration, per cent.	Sodium yellow.			Mercury.					
				Yellow.			Green.		
	α^{20°.	$[\alpha]^{20^\circ}$.	$[M]^{20^\circ}$.	α^{20°.	$[\alpha]^{20^\circ}$.	$[M]^{20^\circ}$.	α^{20°.	$[\alpha]^{20^\circ}$.	$[M]^{20^\circ}$.
2	1·210°	14·74°	100·7°	1·290°	15·72°	107·3°	1·589°	19 37°	132·3°
4	2·421	14·80	101·0	2·560	15·65	106·8	3·171	19·38	132·4
8	4·712	14·66	100·1	5·024	15·63	106·7	6·225	19·37	132·2
16	9·487	14·70	100·4	10·073	15·60	106·6	12·483	19·34	132·1

Concentrations : approximately 2 per cent. : 0·6157 gram in 30·006 c.c. at 20°.
,, 4 ,, 1·2275 ,, ,, ,,
,, 8 ,, 2·4117 ,, ,, ,,
,, 16 ,, 4·8426 ,, ,, ,,

Rotatory dispersions :

Approximate concentration, per cent.	Hg_{yellow}/Na_{yellow}.	Hg_{green}/Na_{yellow}.
2	1·066	1·313
4	1·057	1·310
8	1·066	1·321
16	1·062	1·316
Mean	1·063	1·315

Calcium Salt, $(C_{10}H_{15}O_4S)_2Ca,4H_2O$.

Approximate concentration, per cent.	Sodium yellow.			Mercury.					
				Yellow.			Green.		
	α^{20°.	$[\alpha]^{20^\circ}$.	$[M]^{20^\circ}$.	α^{20°.	$[\alpha]^{20^\circ}$.	$[M]^{20^\circ}$.	α^{20°.	$[\alpha]^{20^\circ}$.	$[M]^{20}$.
2	1·410°	17·22°	98·94°	1·512°	18·47°	106·1°	1·863°	22·76°	130·8°
4	2·773	17·15	98·50	2·964	18·32	105·26	3·667	22·67	130·2
8	5·423	16·91	97·15	5·774	18·00	103·4	7·166	22·35	128·4
16	10·657	16·65	95·67	11·378	17·77	102·12	14·123	22·06	126·75

Concentrations : approximately 2 per cent. : 0·6142 gram in 30·006 c.c. at 20°.
,, 4 ,, 1·2137 ,, ,, ,,
,, 8 ,, 2·4058 ,, ,, ,,
,, 16 ,, 4·8023 ,, ,, ,,

Rotatory dispersions:

Approximate concentration, per cent.	$\mathrm{Hg}_{\text{yellow}}/\mathrm{Na}_{\text{yellow}}$.	$\mathrm{Hg}_{\text{green}}/\mathrm{Na}_{\text{yellow}}$.
2	1·072	1·321
4	1·068	1·322
8	1·065	1·321
16	1·068	1·325
Mean	1·068	1·322

Barium Salt, $(C_{10}H_{15}O_4S)_2Ba,3H_2O$.

Approximate concentration, per cent.	Sodium yellow.			Mercury. Yellow.			Mercury. Green.		
	α^{20°.	$[\alpha]^{20^\circ}$.	$[M]^{20^\circ}$.	α^{20°.	$[\alpha]^{20^\circ}$.	$[M]^{20^\circ}$.	α^{20°.	$[\alpha]^{20^\circ}$.	$[M]^{20^\circ}$.
2	1·209°	15·08°	98·58°	1·310°	16·34°	106·9°	1·603°	20·00°	130·8°
4	2·424	14·98	98·00	2·606	16·11	105·3	3·220	19·89	130·1
8	4·767	14·77	96·64	5·086	15·77	103·1	6·313	19·57	127·9
16	9·114	14·53	95·04	9·710	15·49	101·3	12·064	19·23	125·8

Concentrations: approximately 2 per cent.: 0·6007 gram in 29·979 c.c. at 20°.
,, 4 ,, 1·2141 ,, 30·006 ,, ,,
,, 8 ,, 2·4203 ,, 30·006 ,, ,,
,, 16 ,, 4·7040 ,, 30·006 ,, ,,

Rotatory dispersions:

Approximate concentration, per cent.	$\mathrm{Hg}_{\text{yellow}}/\mathrm{Na}_{\text{yellow}}$.	$\mathrm{Hg}_{\text{green}}/\mathrm{Na}_{\text{yellow}}$.
2	1·083	1·326
4	1·075	1·328
8	1·067	1·324
16	1·065	1·323
Mean	1·072	1·325

Ammonium Salt, $C_{10}H_{15}O_4S \cdot NH_4$.

Approximate concentration, per cent.	Sodium yellow.			Mercury. Yellow.			Mercury. Green.		
	α^{20°.	$[\alpha]^{20^\circ}$.	$[M]^{20^\circ}$.	α^{20°.	$[\alpha]^{20^\circ}$.	$[M]^{20^\circ}$.	α^{20°.	$[\alpha]^{20^\circ}$.	$[M]^{20^\circ}$.
1	0·813°	20·21°	50·38°	0·873°	21·70°	54·09°	1·073°	26·68°	66·50°
2	1·661	20·24	50·45	1·782	21·71	54·12	2·191	26·70	66·55
4	3·297	20·46	51·00	3·512	21·79	54·31	4·354	27·01	67·35
8	6·544	20·46	51·00	6·977	21·81	54·37	8·634	26·99	67·29
16	13·294	20·79	51·85	14·188	22·20	55·34	17·538	27·43	68·39

Concentrations: approximately 1 per cent.: 0·3018 gram in 30·006 c.c. at 20°.
,, 2 ,, 0·6129 ,, ,, ,,
,, 4 ,, 1·2095 ,, ,, ,,
,, 8 ,, 2·3998 ,, ,, ,,
,, 16 ,, 4·7953 ,, ,, ,,

Rotatory dispersions:

Approximate concentration, per cent.	$\text{Hg}_{\text{yellow}}/\text{Na}_{\text{yellow}}$.	$\text{Hg}_{\text{green}}/\text{Na}_{\text{yellow}}$.
1	1·074	1·320
2	1·073	1·319
4	1·065	1·320
8	1·066	1·319
16	1·067	1·319
Mean	1·069	1·319

Piperidine Salt, $C_{10}H_{15}O_4S{\cdot}C_5H_{12}N$.

				Mercury.					
Approximate concentration, per cent.	Sodium yellow.			Yellow.			Green.		
	$\alpha^{20°}$.	$[\alpha]^{20°}$.	$[M]^{20°}$.	$\alpha^{20°}$.	$[\alpha]^{20°}$.	$[M]^{20°}$.	$\alpha^{20°}$.	$[\alpha]^{20°}$.	$[M]^{20°}$.
2	1·303°	15·97°	50·70°	1·390°	17·04°	54·09°	1·699°	20·83°	66·12°
4	(1) 2·423	16·07	51·00	2·619	17·36	55·11	3·229	21·41	67·96
	(2) 2·320	16·18	51·36	2·472	17·24	54·72	3·061	21·34	67·74
		16·12	51·18		17·30	54·91		21·37	67·85
8	5·431	16·50	52·38	5·779	17·56	55·72	7·121	21·63	68·66
16	Solution too concentrated to read for "Na" light			11·061	18·07	57·35	13·645	22·29	70·77

Concentrations : approximately 2 per cent. : 0·6115 gram in 29·979 c.c. at 20°.
,, 4 ,, (1) 1·1305 ,, ,, ,,
(2) 1·0747 ,, ,, ,,
,, 8 ,, 2·4680 ,, ,, ,,
,, 16 ,, 4·5871 ,, ,, ,,

Rotatory dispersions:

Approximate concentration, per cent.	$\text{Hg}_{\text{yellow}}/\text{Na}_{\text{yellow}}$.	$\text{Hg}_{\text{green}}/\text{Na}_{\text{yellow}}$.
2	1·067	1·304
4	1·073	1·325
8	1·064	1·311
Mean	1·068	1·313

Summary of Rotatory Dispersions (mean values) of the Salts of d-*Camphor-β-sulphonic Acid.*

	$\text{Hg}_{\text{yellow}}/\text{Na}_{\text{yellow}}$.	$\text{Hg}_{\text{green}}/\text{Na}_{\text{yellow}}$.
Zinc	1·064	1·315
Magnesium	1·064	1·315
Cadmium	1·063	1·315
Calcium	1·068	1·322
Barium	1·072	1·325
Ammonium	1·069	1·319
Piperidine	1·068	1·313

From these results it is evident that there is practically no change in rotatory dispersion with change of concentration, and that the mean rotatory dispersions for the different salts are practically identical.

Lead Salt.—This salt was also prepared, but as it decomposed rather readily in aqueous solution into a white, insoluble compound, presumably a basic salt, its rotatory power was not examined.

Rotatory Powers and Rotatory Dispersions of other derivatives of d-*Camphor-β-sulphonic Acid, with Chloroform as Solvent.*

The chloride, amide, and anhydramide of this acid were prepared in the manner described by Reychler (*Bull. Soc. chim.*, 1898, [iii], **19**, 120) and Armstrong and Lowry (Trans., 1902, **81**, 1448), except that in the preparation of the chloride the ammonium salt was employed instead of the free acid. The piperidide was obtained from the chloride and piperidine by the Schotten-Baumann reaction.

d-*Camphor-β-sulphonyl Chloride.*—This compound was in the first place recrystallised from dry ether, but as the purified substance after a short time showed signs of decomposition, dry benzene was subsequently employed as solvent, on crystallisation from which the chloride appeared to decompose less easily.

Two solutions were made up with purified chloroform, the strength of the solutions being approximately 4 per cent. The polarimetric results were as follows:

				Mercury.					
	Sodium.			Yellow.			Green.		
	$\alpha^{20°}$.	$[\alpha]^{20°}$.	$[M]^{20°}$.	$\alpha^{20°}$.	$[\alpha]^{20°}$.	$[M]^{20°}$.	$\alpha^{20°}$.	$[\alpha]^{20°}$.	$[M]^{20°}$.
I	4·516°	32·14°	80·54°	4·740°	33·73°	84·51°	5·598°	39·83°	99·83°
II	4·892	32·21	80·71	5·178	34·09	85·43	6·125	40·34	101·10
Mean		32·17	80·62		33·91	84·97		40·08	100·46

I. 1·0533 gram of chloride in 29·979 c.c. of chloroform at 20°.
II. 1·1385 ,, ,, ,, ,, ,,

Mean rotatory dispersions:

$$\mathrm{Hg}_{\text{yellow}}/\mathrm{Na}_{\text{yellow}} = 1·054\,; \quad \mathrm{Hg}_{\text{green}}/\mathrm{Na}_{\text{yellow}} = 1·245.$$

d-*Camphor-β-sulphonamide*, $C_{10}H_{15}O\cdot SO_2\cdot NH_2$.—This compound was purified by repeated crystallisation from hot water, and finally twice from alcohol. The amide was thus obtained in a state of purity, but when polarimetric readings were made with material preserved in a stoppered bottle for four or five weeks, the substance had decomposed largely into the anhydramide.

As only a small amount of the pure amide had been obtained, owing to its ready conversion into the anhydramide, this compound was not examined polarimetrically.

As an instance of the ease with which the amide is transformed into the anhydramide, it may be remarked that, on boiling an aqueous solution of the former, a deposit of the nearly insoluble anhydramide is formed. On keeping over anhydrous calcium chloride in a desiccator for a few days, the amide is converted practically completely into the anhydramide.

d-*Camphor-β-sulphonanhydramide*, $C_{10}H_{15}O_2NS$.—This compound was purified by repeated crystallisation from boiling alcohol, when it melted at 223°. Two approximately 2 per cent. solutions, with chloroform as solvent, were examined, with the following results:

					Mercury.				
	Sodium.			Yellow.			Green.		
	α^{20°.	$[\alpha]^{20^\circ}$.	$[M]^{20^\circ}$.	α^{20°.	$[\alpha]^{20^\circ}$.	$[M]^{20^\circ}$.	α^{20°.	$[\alpha]^{20^\circ}$.	$[M]^{20^\circ}$.
I.	−3·048°	−33·83°	−72·15°	−3·073°	−34·10°	−72·74°	−3·450°	−38·29°	−81·66°
II.	3·080	33·76	71·99	3·162	34·65	73·90	3·543	38·83	82·80
Mean ...		−33·79	−72·07		−34·37	−73·32		−38·56	−82·23

I. 0·6753 gram in 29·979 c.c. of chloroform at 20°
II. 0·6840 ,, ,, ,, ,,

Mean rotatory dispersions:

$$\mathrm{Hg_{yellow}/Na_{yellow}} = 1{\cdot}017\ ; \quad \mathrm{Hg_{green}/Na_{yellow}} = 1{\cdot}141.$$

Piperidide.—The two compounds formulated by Armstrong and Lowry (Trans., 1902, **81**, 1449) as piperidides, and later by Lowry and Magson (Trans., 1906, **89**, 1050) as normal piperidide and piperido-lactone respectively, were prepared by the Schotten-Baumann reaction. The compound of low melting point was obtained as an oil, and was separated from the other substances present in the mixture by repeated extraction with water, the piperidide being insoluble. This oil is exceedingly difficult to crystallise, and success in this respect was only attained by cooling it in liquid air. The oil solidified, but on attaining the temperature of the laboratory again, appeared to revert to the original condition of an oil. However, on keeping overnight, it was found that the supercooled oil had crystallised out as a solid mass of crystals. These were collected and washed with light petroleum (b. p. 30—40°), and then dried on a porous plate. This compound is not very soluble in light petroleum, but crystallisation takes place more easily from this solvent than from any other. In the case of almost any other solvent the impure piperidide is left as a gummy mass, which crystallises only after a considerable time.

The piperidide of low melting point was thus purified by repeated crystallisation from light petroleum, the crystals being powdered and washed with light petroleum after each crystallisation. They were dried on a porous plate, and again crystallised from light petroleum. As the melting point during the last couple of crystallisations remained practically constant (and sharp) at 46—47°, this purified sample was examined polarimetrically, with the following results:

Solvent: Chloroform.

				Mercury.					
	Sodium.			Yellow.			Green.		
	$\alpha^{20°}$.	$[\alpha]^{20°}$.	$[M]^{20°}$.	$\alpha^{20°}$.	$[\alpha]^{20°}$.	$[M]^{20°}$.	$\alpha^{20°}$.	$[\alpha]^{20°}$.	$[M]^{20°}$.
I	0·762°	33·45°	100·15°	0·818°	35·91°	107·5°	0·970°	42·58°	127·5°
II	1·292	33·38	99·90	1·389	35·88	107·4	1·644	42·46	127·1
Mean		33·41	100·02		35·89	107·4		42·52	127·3

Concentrations: I. 0·1708 gram in 29·979 c.c. of chloroform at 20°.
II. 0·2903 ,, ,, ,, ,,

(Armstrong and Lowry give $[\alpha]_D^{10} = 33·6°$, for a concentration of 10 grams in 100 c.c. of chloroform.)

Mean rotatory dispersions:

$$Hg_{yellow}/Na_{yellow} = 1·074; \quad Hg_{green}/Na_{yellow} = 1·272.$$

The second compound produced in the reaction between the acid chloride and piperidine, melting at 140° and formulated by Lowry and Magson as the piperido-lactone, was isolated from the aqueous solution by evaporation to dryness, extracting the residue with chloroform, evaporating again to dryness, and extracting with acetone. The latter solution on evaporation leaves a brown, oily mass, which on cooling and stirring with a little light petroleum suddenly becomes solid. On recrystallising twice from acetone, a sample melting at 136—137° was obtained.

In the meantime the piperidine salt of *d*-camphor-β-sulphonic acid described above had been prepared and purified by recrystallisation from acetone. This compound melted at 140°, and appeared to be identical in properties with the so-called piperido-lactone isolated from the piperidide preparation. The identity was confirmed by the value obtained for the specific rotation in chloroform solution, this value being practically identical with that obtained by Armstrong and Lowry. That this compound, prepared as the piperidine salt, was really such was proved by the following facts:

(1) Sodium hydroxide in the cold liberates piperidine from an aqueous solution of the compound.

(2) Combustion results, given above, agree with the formula for the piperidine salt, no water of crystallisation being present, and not with the figures required for a piperidide or piperido-lactone.

(3) The molecular rotatory powers and rotatory dispersions of the compound in aqueous solution correspond in value with the figures obtained for the ammonium salt.

It is therefore evident that the compound melting at 140° isolated in the preparation of the piperidide is in reality the piperidine salt of *d*-camphor-β-sulphonic acid, and not a piperido-lactone of this acid.

As the compound described as α-bromocamphor-β-sulphopiperidolactone (m. p. 123°) (Armstrong and Lowry, Trans., 1902, **81**, 1452; Lowry and Magson, Trans., 1906, **89**, 1051) yields the above compound, namely, the piperidine salt of *d*-camphor-β-sulphonic acid, on reduction, it is intended to examine it and the piperidine salt of α-bromocamphor-β-sulphonic acid.

Rotatory Power of Piperidine d-*Camphor-β-sulphonate in Chloroform.*

	Sodium.			Mercury.					
				Yellow.			Green.		
	α^{20°.	$[\alpha]^{20^\circ}$.	$[M]^{20^\circ}$.	α^{20°.	$[\alpha]^{20^\circ}$.	$[M]^{20^\circ}$.	α^{20°.	$[\alpha]^{20^\circ}$.	$[M]^{20^\circ}$.
I	2·027°	32·37°	102·8°	2·188°	34·94°	110·9°	2·593°	41·40°	131·4°
II	1·175	32·08	101·9	1·248	34·06	108·2	1·485	40·54	128·7
Mean		32·22	102·3		34·50	109·6		40·97	130·0

I. 0·4694 gram in 29·979 c.c. of chloroform at 20°.
II. 0·2747 ,, 30·0 ,, ,, ,,

Mean rotatory dispersions:

$Hg_{yellow}/Na_{yellow} = 1·071$; $Hg_{green}/Na_{yellow} = 1·271$.

A sample of the pure acid was obtained from the purified ammonium salt by preparing the barium salt, and exactly precipitating the barium as sulphate; the filtered solution was evaporated to dryness, and the acid then crystallised three times from dry acetone. The resulting product was found to lose an amount in weight at 100° corresponding with $1H_2O$. A titration of the solution of a weighed amount of acid also pointed to the formula $C_{10}H_{15}O\cdot SO_3H,H_2O$. When, however, these crystals were examined polarimetrically, the different results obtained for the specific and molecular rotations from two samples showed that the acid had absorbed varying amounts of water. As, however, the rotatory dispersions are independent of the weight of active substance, the figures for these are given. The solutions were approximately 1 per cent. in chloroform at 20°.

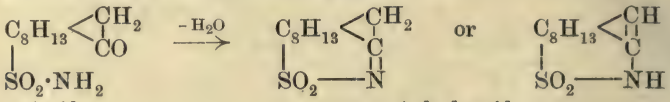
A comparison of the rotatory dispersions of the derivatives of *d*-camphor-β-sulphonic acid is made in the following table:

Rotatory Dispersions in Chloroform at 20°.

	Hg_{yellow}/Na_{yellow}.	Hg_{green}/Na_{yellow}.
d-Camphor-β-sulphonic acid......... (Mean of two determinations)	1·056	1·274
d-Camphor-β-sulphonyl chloride ...	1·054	1·245
,, piperidide.	1·074	1·272
Piperidine *d*-camphor-β-sulphonate	1·071	1·271
d-Camphor-β-sulphonanhydramide	1·017	1·141

These figures indicate that there is comparatively little difference in rotatory dispersions between the acid, its chloride, piperidide, and piperidine salt; it will be noted that the figures for the piperidide and piperidine salt are practically identical, and from this it may be deduced that the configuration, formulated by Lowry and Magson for the former compound as the true piperidide, is the correct one.

Again, it will be noticed that the anhydramide differs considerably in rotatory dispersions from the other derivatives of camphorsulphonic acid; this is as might be expected from the change of configuration produced by the linking up of the nitrogen atom with the carbon atom of the carbonyl group, thus:



Amide. Anhydramide.

The residual solution obtained from the preparation of the crystalline "Reychler" camphorsulphonic acid, and described by Reychler (*Bull. Soc. chim.*, 1898, [iii], **19**, 127) as containing an amorphous acid, is at present the subject of further investigation. Evidence has, however, been obtained, showing that there are at least two other compounds present, one of which has been isolated, besides a certain amount of *d*-camphor-β-sulphonic acid, which remains in solution, and which thus renders the isolation of a second acid from the residual solution more difficult.

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LXXXI.—*The Externally Compensated and Optically Active Hydroxyhydrindamines, their Salts and Derivatives.*

By WILLIAM JACKSON POPE and JOHN READ.

THE introduction of the optically active camphor- and bromocamphor-sulphonic acids as agents for the resolution of externally compensated bases (Pope and Peachey, Trans., 1898, **73**, 893) has led to the production of basic substances, the optical activity of which is associated with the presence in the molecule of an asymmetric nitrogen, phosphorus, sulphur, selenium, silicon, tin, cobalt, chromium, or iron atom; it has further greatly facilitated the resolution of basic compounds containing an asymmetric carbon atom. At the outset of this work it was indicated that the acids in question might be expected to prove of value for the resolution of externally compensated bases, because they differed from acids previously used for that purpose in being very powerful acids, in yielding highly crystalline salts, and in giving salts of such general sparing solubility that the ordinary laws governing the separation of salts from complex solutions could be readily applied (Pope and Peachey, Trans., 1899, **75**, 1066).

Although the number of optically active bases applicable in the resolution of externally compensated acids is far greater than the number of optically active acids available for the resolution of externally compensated bases, a little consideration will show that no optically active base is known of which the properties conform to those of the camphor- and bromocamphor-sulphonic acids. That is to say, we possess no very powerful and optically active base which is easily obtainable, and the salts of which exhibit a tendency towards crystallising well and towards being sparingly soluble. As the introduction of such a base would be expected to facilitate the resolution of externally compensated acids and to lead to progress in that direction comparable to that which has been achieved with externally compensated bases, we have for some years been occupied in searching for a base possessing properties of the kind described.

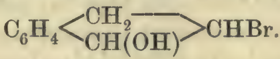
The optically active hydroxyhydrindamines appear to answer the conditions laid down. The *d*- and *l*-isomerides are easily obtainable in quantity by the methods described below, their salts in general crystallise remarkably well, and are usually very sparingly soluble in certain organic solvents, and the bases themselves are solid, crystalline substances. These bases are comparatively powerful ones; they form stable carbonates, liberate ammonia from its salts, and precipitate the hydroxides of certain of the heavy metals from salt solutions. In the present paper we describe the preparation of the bases and the properties of a number of their salts and derivatives; we also establish the molecular rotation constants of the salts in aqueous and other solutions.

It will be noticed that the bases and many of their salts exhibit a very remarkable mutarotation in alcoholic and acetone solutions; this mutarotation is most marked in the bases themselves and in their salts with feeble acids, and, as hydroxyhydrindamine is a fully saturated substance, we can at present offer no suggestion as to its cause. The progress of the mutarotation is frequently marked by the development of a brown colour and the production of a brown, resinous matter on evaporating the solution; but most of the material can in general be recovered unchanged from these residues.

For the first time attention is drawn in the present paper to the occurrence of a curious discrepancy between the observed rotatory powers of salts formed between optically active acids and bases and the values deduced from observations made with inorganic salts of the optically active base or acid. It is shown with the salts which *d*- and *l*-hydroxyhydrindamine form with *a*-bromocamphor-π-sulphonic acid and β-camphorsulphonic acid that whilst the molecular rotatory powers in aqueous solutions of the salts *lBdA* can be calculated with great exactness from the molecular rotatory powers of the corresponding hydrochlorides of the bases and the ammonium salts of the acids, this cannot be done with the salts of the composition *dBdA*; the discrepancy in the latter case is very large. The same sort of behaviour is observed with the bromocamphorsulphonates of *d*- and *l*-tetrahydroquinaldine. Further experience with other optically active bases will show whether it is a general rule that the salts *lBdA* behave normally and the salts *dBdA* abnormally in respect to molecular rotatory power in aqueous solution.

EXPERIMENTAL.

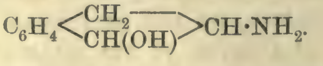
Externally Compensated 2-*Bromo*-1-*hydroxyhydrindene*,



$$C_6H_4\left<\begin{matrix}CH_2\text{——}\\CH(OH)\end{matrix}\right>CHBr.$$

The following method of preparation of this substance represents a considerable improvement on that which we have previously given (Trans., 1911, **99**, 2071). Indene (40 grams) is well emulsified in water (1 litre) at 90° contained in a capacious flask; the mixture is then well agitated with successive small quantities of bromine dissolved in potassium bromide solution (5 per cent.), the addition being continued until the colour of the bromine persists. A quantity of bromohydroxyhydrindene crystallises out during this operation, and, after cooling, the deposit is collected and washed with light petroleum, which removes a small quantity of a pale yellow oil; the product is finally purified by crystallisation from aqueous alcohol. The yield obtained is about 85 per cent. of the theoretically possible one.

Externally Compensated 1-*Hydroxy*-2-*hydrindamine*,



$$C_6H_4\left<\begin{matrix}CH_2\text{——}\\CH(OH)\end{matrix}\right>CH\cdot NH_2.$$

This base is prepared in the manner previously described for obtaining dihydroxydihydrindamine together with hydroxyhydrindamine (*loc. cit.*, 2074); when the maximum proportion of the latter base is required it is convenient to increase the quantity of ammonia with which the bromohydroxyhydrindene is shaken. The yield of pure recrystallised hydroxyhydrindamine may be thus increased to 65 per cent. of the theoretical, that of dihydrodihydrindamine being correspondingly diminished. The crude base possesses a pale yellow colour, and is purified by crystallisation from boiling water, which dissolves it freely, or from boiling benzene, in which it is sparingly soluble. For most purposes, and in order to get rid of all the colour, it is convenient to purify the product by dissolving it in acetone, and adding slightly more than the calculated quantity of concentrated hydrochloric acid; the hydrochloride is then deposited in a pure, colourless condition, being almost quantitatively insoluble in the acetone solution. The physical properties of the base have been already described; it is moderately soluble in cold water, and, in the crystalline condition, does not absorb carbon dioxide from the air.

The *hydrochloride*, $C_9H_9O{\cdot}NH_2,HCl$, prepared as above indicated and recrystallised from aqueous acetone, is obtained in glistening, white scales. It is readily soluble in water, is precipitated from its aqueous solutions by addition of hydrochloric acid, is very sparingly soluble in alcohol, and practically insoluble in dry acetone:

0·2799 required 15·1 c.c. $N/10\text{-}AgNO_3$. Cl = 19·13.

$C_9H_{11}ON,HCl$ requires Cl = 19·11 per cent.

The *sulphate*, $(C_9H_9O{\cdot}NH_2)_2,H_2SO_4$, separates on adding the requisite amount of sulphuric acid to an acetone solution of the base; it is sparingly soluble in acetone, moderately so in boiling water, and crystallises from the latter solvent in well-developed prisms:

0·4103 gave 0·2434 $BaSO_4$. $SO_4 = 24·41$.

$(C_9H_{11}ON)_2,H_2SO_4$ requires $SO_4 = 24·24$ per cent.

The *nitrate* is obtained as a highly crystalline powder on adding concentrated nitric acid to an ethyl acetate solution of the base; it is extremely soluble in water.

The *picrate*, $C_9H_9O{\cdot}NH_2,C_6H_2(NO_2)_3{\cdot}OH$, is readily soluble in warm acetone, from which it crystallises in fine, yellow needles. It is sparingly soluble in boiling water or alcohol, and crystallises from hot water in long, yellow needles melting at 227°:

0·2135 gave 0·3735 CO_2 and 0·0720 H_2O. C = 47·71; H = 3·79.

$C_9H_{11}ON,C_6H_3O_7N_3$ requires C = 47·60; H = 3·73 per cent.

The *carbonate*, $(C_9H_9O{\cdot}NH_2)_2,H_2CO_3$, is precipitated as a white, amorphous powder on passing carbon dioxide into solutions of the base in acetone or water, or by adding a solution of an alkali carbonate to aqueous solutions of a salt of the base. The salt appears to be stable in the air, although on exposing the free base to the air for three months it could not be found to have absorbed carbon dioxide; on heating in contact with water or acetone it decomposes with evolution of carbon dioxide. It melts and blackens at about 132°. When the carbonate is precipitated by passing carbon dioxide through strong solutions of the base in acetone or water, it is found to contain too much carbon and too little hydrogen, as will be seen from the accompanying analyses made on specimens prepared from such solutions in acetone and water respectively; although it was at first thought that this might be due to the formation of an anhydrocarbonate or of a carbamate, the real cause is probably to be found in the retention of free base by the precipitated salt. This conclusion is confirmed by analyses made on the carbonate of the *d*-base and quoted below:

0·2265 gave 0·5495 CO_2 and 0·1315 H_2O. $C=66·16$; $H=6·50$.
0·2196 „ 0·5275 CO_2 „ 0·1250 H_2O. $C=65·51$; $H=6·37$.
$(C_9H_{11}ON)_2,H_2CO_3$ requires $C=63·30$; $H=6·72$ per cent.

The production of an insoluble carbonate by passing carbon dioxide through the aqueous solution of an amine or by the addition of an alkali carbonate to the aqueous solution of a salt of the base is probably unique; it is doubtless in part connected with the strength of the base, and in this connexion it should be noted that the base expels ammonia from ammonium chloride solution and precipitates ferric, chromium, and aluminium hydroxides from solutions of the corresponding metallic salts. The solutions of the base are strongly alkaline towards litmus and those of such salts as the hydrochloride are neutral.

The *sulphide* is precipitated as a yellow, amorphous powder on passing hydrogen sulphide through a solution of the base in benzene; it is not precipitated from aqueous solution, and decomposes on exposure to the air with slow evolution of hydrogen sulphide. In view of the latter fact it was not analysed; the salt melts at 125° with blackening.

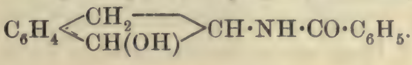
The *acetate*, $C_9H_9O\cdot NH_2,C_2H_4O_2$, separates on adding glacial acetic acid to an acetone solution of the base; it is readily soluble in warm acetone, and crystallises from the solution in soft, feathery needles, melting at about 128° with blackening. The salt is extremely soluble in water or alcohol, and dissolves sparingly in ethyl acetate; it and the following two salts were prepared for comparison with the corresponding salts of the optically active bases, to which an especial interest attaches:

0·1895 gave 0·4340 CO_2 and 0·1240 H_2O. $C=62·46$; $H=7·32$.
$C_9H_{11}ON,C_2H_4O_2$ requires $C=63·12$; $H=7·23$ per cent.

The *benzoate*, prepared from silver benzoate and hydroxyhydrindamine hydrochloride, crystallises from hot acetone, in which it is moderately soluble, in small, glistening scales, melting at about 165° with blackening. It is extremely soluble in water.

The *salicylate*, prepared in a similar manner, is even more soluble than the benzoate in acetone or water; it crystallises from a mixture of acetone and ethyl acetate in small, white needles melting at 182°. No aurichloride could be prepared because auric chloride is reduced by solutions of the base or its salts.

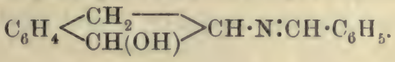
dl-1-*Hydroxy-2-benzoylhydrindamide*,


$C_6H_4<\begin{matrix}CH_2\\CH(OH)\end{matrix}>CH\cdot NH\cdot CO\cdot C_6H_5.$

The benzoyl derivative, obtained by the Schotten-Baumann method, is readily soluble in hot alcohol, and crystallises in soft, silky scales melting at 203°:

0·1597 gave 0·4427 CO_2 and 0·0864 H_2O. C = 75·65; H = 6·05.
$C_{16}H_{15}O_2N$ requires C = 75·85; H = 5·97 per cent.

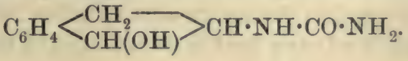
dl-1-*Hydroxy-2-benzylidenehydrindamine*,


$C_6H_4<\begin{matrix}CH_2\\CH(OH)\end{matrix}>CH\cdot N:CH\cdot C_6H_5.$

This substance is formed in theoretical yield on mixing the base with benzaldehyde, heat being evolved in the reaction. It is readily soluble in hot acetone, alcohol, or ethyl acetate, but sparingly so in benzene or chloroform, and crystallises from acetone in small, glistening prisms melting at 166°:

0·1716 gave 0·5093 CO_2 and 0·0978 H_2O. C = 80·94; H = 6·32.
$C_{16}H_{15}ON$ requires C = 80·97; H = 6·38 per cent.

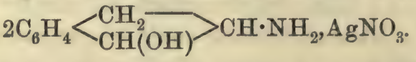
dl-1-*Hydroxy-2-carbamidohydrindamine*,


$C_6H_4<\begin{matrix}CH_2\\CH(OH)\end{matrix}>CH\cdot NH\cdot CO\cdot NH_2.$

This compound is formed as a copious, white precipitate on adding potassium cyanate solution to a solution of a salt of the base. It is very sparingly soluble in water or alcohol, and practically insoluble in all the other usual solvents with the exception of glacial acetic acid, which dissolves it freely. The substance crystallises from a large amount of boiling water in very fine, lustrous needles melting at 233°, and is very stable, being unaffected by boiling with concentrated potassium hydroxide solution; with excess of strong mineral acids it forms crystalline salts, which are hydrolysed on the addition of water:

0·1605 gave 0·3665 CO_2 and 0·0905 H_2O. C = 62·28; H = 6·31.
$C_{10}H_{12}O_2N_2$ requires C = 62·46; H = 6·30 per cent.

dl-1-*Hydroxy-2-hydrindamine Silver Nitrate,*



$$2C_6H_4{<}\begin{matrix}CH_2\text{——}\\CH(OH)\end{matrix}{>}CH\cdot NH_2,AgNO_3.$$

On addition of silver nitrate solution to a concentrated aqueous solution of the base a copious, white precipitate separates; when precipitation is complete the precipitate is collected, washed with cold water, and crystallised from warm water. The compound is thus obtained in long, white needles, which, when dry, decompose at about 120°, and only change colour very slowly on exposure to bright sunlight; the aqueous solution decomposes at about 50°, with formation of an excellent silver mirror on the surface of the glass vessel:

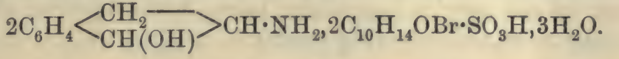
0·3704 gave 0·0846 Ag. Ag = 22·84.
$(C_9H_{11}ON)_2,AgNO_3$ requires Ag = 23·05 per cent.

Compounds similar to the above appear to be formed on mixing solutions of hydroxyhydrindamine with aqueous solutions of other metallic salts, such as copper sulphate, nickel sulphate, and cobalt nitrate. This production in aqueous solution of stable compounds between a primary amine and a metallic salt appears to be rare, and it will be noticed that the composition of the silver nitrate compound corresponds with that of the more stable of the additive compounds, $AgNO_3,2NH_3$, formed between this salt and ammonia; Wolff has prepared (*Ber.*, 1893, **26**, 724) a double compound, $C_4H_4N_2,AgNO_3$, of pyrazine and silver nitrate, which can be crystallised from hot water without decomposition. We purpose carefully investigating the new class of additive compounds obtained from *dl*-hydroxyhydrindamine, and preparing the corresponding substances from *d*- and *l*-hydroxyhydrindamine; the determination of the rotation constants of the latter substances should elucidate the nature of such double compounds in general.

The Resolution of dl-*Hydroxyhydrindamine.*

Externally compensated hydroxyhydrindamine is conveniently resolved into its optically active components by the aid of the equilibrium method of Pope and Peachey (Trans., 1899, **75**, 1066). Two molecular proportions of the externally compensated hydrochloride (55·7 grams) are dissolved in water (300 c.c.), and to the warm solution is added a concentrated aqueous solution of slightly less than one molecular proportion of ammonium *d*-*α*-bromocamphor-*π*-sulphonate (48 grams). The solution does not crystallise on cooling, and requires to be inoculated with solid salt; the latter was obtained in the first instance by evaporating a little of the solution to a syrup, and allowing the residue to separate slowly from its solution in pure ethyl acetate. In subsequent operations crystallisation was induced by inoculation, either with the *d*-*α*-bromocamphor-*π*-sulphonate of the *l*-base or the enantiomorphously related salt. After inoculation a rapid and copious separation of long, glistening needles occurs.

l-*Hydroxy-2-hydrindamine* d-*α-Bromocamphor-π-sulphonate*,



$$2C_6H_4{<}\begin{matrix}CH_2\\CH(OH)\end{matrix}{>}CH\cdot NH_2,2C_{10}H_{14}OBr\cdot SO_3H,3H_2O.$$

After being twice recrystallised from boiling water the salt is found to be pure, and to consist of *l*-hydroxy-2-hydrindamine *d*-*α*-bromocamphor-*π*-sulphonate; the yield of pure salt thus obtained (47 grams) amounts to 70 per cent. of that theoretically possible. The compound dissolves readily in hot water, and is deposited on cooling in magnificent, transparent prisms, which are often twinned and are frequently an inch in length. It melts at 221°, and in a saturated acetone solution gives a precipitate of the hydrochloride on addition of hydrochloric acid; the sulphate is not deposited on addition of sulphuric acid to the acetone solution. It dissolves readily in hot alcohol, is sparingly soluble in hot ethyl acetate, and but very slightly so in hot benzene or acetone:

0·2155 gave 0·3710 CO_2 and 0·1155 H_2O. $C=46·95$; $H=5·79$.
0·2015 „ 0·3470 CO_2 „ 0·1055 H_2O. $C=46·97$; $H=5·86$.
$C_9H_{11}ON,C_{10}H_{15}O_4BrS,1·5H_2O$ requires $C=46·79$; $H=6·00$ per cent.
$C_9H_{11}ON,C_{10}H_{15}O_4BrS,H_2O$ requires $C=47·67$; $H=5·90$ per cent.

The salt does not lose water at 100°, and it will be seen that combustion analysis is not sufficiently delicate to allow of a definite conclusion as to whether the salt contains one or one and a-half molecules of water of crystallisation; the latter proportion is assumed in calculating the molecular rotatory powers given below.

d-*Hydroxyhydrindamine* l-*α-Bromocamphor-π-sulphonate.*

After the separation of the major portion of the *l*-base in the manner just described, the mixed mother liquors from resolution and recrystallisation are evaporated to a small bulk, and the residual crude *d*-base precipitated by addition of very concentrated potassium hydroxide; the precipitate is collected, dissolved in warm acetone, the solution filtered, and a slight excess of concentrated hydrochloric acid added. The hydrochloride of the mixture of bases, containing excess of the *d*-component, then separates quantitatively in a pure condition, and, by a determination of rotatory power, the quantity of *d*-base which it contains is ascertained. The hydrochloride is now dissolved in warm water, and treated with slightly less than the calculated requisite amount of ammonium *l*-α-bromocamphor-π-sulphonate to combine with all the *d*-base; after inoculation and treatment as before, *d*-hydroxyhydrindamine *l*-α-bromocamphor-π-sulphonate, the salt enantiomorphously related to the one previously described, is obtained in a yield of over 70 per cent. The ordinary properties of the new salt are identical with those of the previously described one, and do not call for separate description; the rotation constants of the salt of the *d*-base have, however, been carefully determined, with the following results:

	0·2292 gram in water.			0·4530 gram in water.		
	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α	−1·72°	−1·45°	−1·39°	−3·40°	−2·88°	−2·73°
[α] ...	56·3	47·5	45·5	56·3	47·7	45·2
[M] ...	274	231	222	274	232	220
Rotatory dispersions :	1·237 ; 1·043.			1·245 ; 1·055.		

In all the determinations of rotatory power given in this paper the weight of material stated was made up to 30 c.c. at 20° with the solvent and the solution examined at 20° in a 4-dcm. tube. The first rotatory dispersion stated is always for Hg_{green}/Na_{yellow} and the second for Hg_{yellow}/Na_{yellow}.

The values of the molecular rotatory powers for the three wavelengths, calculated from those given below for the hydrochloride of the base and the known values for the ammonium salt of the acid (Pope and Read, Trans., 1910, **97**, 2201), are respectively −275°, −232°, and −218°. No mutarotation was observed in the aqueous solutions, but the following values indicate marked mutarotation in acetone solution; the time stated represents the period between the time of making up the solution and observing the rotations:

0·1239 gram in acetone.

	Time: 30 minutes.			Time: 25 hours.		
	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α	−0·65°	−0·53°	−0·50°	−0·60°	−0·48°	−0·46°
[α]......	39·4	32·1	30·3	36·3	29·1	27·9
[M] ...	192	156	148	177	142	136
Rotatory dispersions :	1·300 ; 1·060.			1·304 ; 1·043.		

	Time: 43 hours.			Time: 98 hours.		
α	−0·62°	−0·51°	−0·48°	−0·67°	−0·54°	−0·51°
[α]......	37·5	30·9	29·1	40·6	32·7	30·9
[M] ...	183	150	142	198	159	150
Rotatory dispersions :	1·292 ; 1·063.			1·314 ; 1·059.		

The determinations of *α* may be taken as correct to 0·01°, so that no doubt exists as to the reality of the mutarotation.

d(or l)-1-*Hydroxy-2-hydrindamine* d(or l)-*α-Bromocamphor-π-sulphonate*, $C_9H_9O \cdot NH_2, C_{10}H_{14}OBr \cdot SO_3H, H_2O$.

These salts are conveniently prepared from the corresponding bases and acids by concentrating the mixed solution on the water-bath until crystallisation occurs. They are extremely soluble in water or alcohol, but may be purified by recrystallisation from ethyl acetate, and then form small, colourless needles melting at 152°:

0·6096 lost 0·0149 at 100° for three hours. $H_2O = 2·28$.

0·2035, dried at 100°, gave 0·3710 CO_2 and 0·1055 H_2O. C = 49·72; H = 5·80.

$C_9H_{11}ON, C_{10}H_{15}O_4BrS, H_2O$ requires $H_2O = 3·78$ per cent.

$C_9H_{11}ON, C_{10}H_{15}O_4BrS$ requires C = 49·54; H = 5·69 per cent.

The following determinations of rotatory power were made:

0·0821 gram in water.

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α……	+0·91°	+0·78°	+0·73°
[*α*] …	83·1	71·3	66·7
[M]…	383	328	307

Rotatory dispersions: 1·247; 1·068.

0·2394 gram in water.

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α……	+2·65°	+2·26°	+2·14°
[*α*] …	83·0	70·8	67·0
[M]…	382	326	307

1·238; 1·056.

0·4776 gram in water.

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α……	+5·38°	+4·58°	+4·35°
[*α*] …	84·5	71·9	68·3
[M]…	389	331	314

Rotatory dispersions: 1·237; 1·053.

0·2338 gram in acetone (95%).

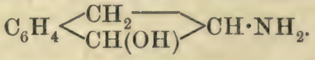
	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α……	+2·97°	+2·53°	+2·39°
[*α*] …	95·3	81·2	76·7
[M]…	439	374	353

1·243; 1·059.

The mean values in aqueous solutions are: $[M]_{Hg\,green} + 383°$; $[M]_{Hg\,yellow} + 327°$; $[M]_{Na\,yellow} + 307°$. No mutarotation was observed in aqueous solution, and only very slight indications of its occurrence were obtained in solutions in acetone diluted with 5 per cent. of water.

The completely externally compensated salt, dl-*hydroxyhydrindamine* dl-*α-bromocamphor-π-sulphonate*, was prepared by mixing the two salts, *dAlB* and *lAdB*, in concentrated aqueous solution and evaporating; it crystallised in stout, lustrous prisms melting at 182°, and is much more soluble than the salts *dAlB* and *lAdB*, but considerably less soluble than the salts *dAdB* and *lAlB*.

d(or l)-1-*Hydroxy-2-hydrindamine*,



$$C_6H_4\Big<\begin{matrix}CH_2\text{———}\\CH(OH)\end{matrix}\Big>CH\cdot NH_2.$$

The optically active bases are most readily prepared by dissolving the salts obtained in the resolution, *lBdA* and *dBlA*, in hot absolute alcohol, and adding the calculated quantity of concentrated hydrochloric acid; the corresponding optically active hydrochloride then separates quantitatively, and is collected and washed with acetone. The strong aqueous solution of the hydrochloride is decomposed by addition of very concentrated potassium hydroxide, and the precipitated base purified by crystallisation from a small quantity of hot water. The active bases crystallise from boiling benzene, in which they are very sparingly soluble, in lustrous, colourless needles several inches in length; they are less soluble than the corresponding externally compensated amine, and melt 14° higher, namely, at 142°:

0·1012 gave 0·2679 CO_2 and 0·0673 H_2O. C = 72·20; H = 7·44.

$C_9H_{11}ON$ requires C = 72·43; H = 7·44 per cent.

After the optically active hydrochlorides have been precipitated from the alcoholic solutions by addition of hydrochloric acid, the mother liquors are evaporated to dryness with ammonia, and the ammonium α-bromocamphor-π-sulphonate recovered by crystallisation. During the resolution there is thus practically no loss either of the amine or of the optically active acids used in its resolution.

The following determinations of the rotation constants were made with pure *d*-hydroxyhydrindamine:

	0·1594 gram in water.			0·3309 gram in water.		
	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.
α	+0·59°	+0·51°	+0·48°	+1·23°	+1·07°	+1·01°
[α]	27·8	24·0	22·6	27·9	24·3	22·9
[M] ...	41·4	35·8	33·7	41·6	36·2	34·1
Rotatory dispersions:	1·229 ; 1·063.			1·218 ; 1·059.		

No mutarotation was observed in aqueous solutions, but solutions in acetone exhibit marked mutarotation; further, the specific rotatory power of the base is about twelve times as great in acetone as in aqueous solutions. In view of this remarkable behaviour of the optically active hydroxyhydrindamines, it is desirable to record the following determinations of rotatory power selected from a very large number which have been made.

(1) 0·1600 gram in acetone.

	Time : 0·5 hour.			Time : 20 hours.		
	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.
α......	+7·30°	+6·33°	+6·04°	+7·20°	+6·24°	+5·94°
$[\alpha]$ ...	342	297	283	338	293	278
[M]...	510	442	422	503	436	415
Rotatory dispersions :	1·209 ; 1·048.			1·212 ; 1·051.		

	Time : 90 hours.			Time : 110 hours.		
α......	+6·98°	+6·05°	+5·76°	+6·92°	+5·98°	+5·71°
$[\alpha]$ ...	327	284	270	324	280	268
[M]...	488	423	403	484	418	399
Rotatory dispersions :	1·212 ; 1·050.			1·212 ; 1·047.		

(2) 0·3159 gram in acetone.

	Time : 100 minutes.			Time : 23 hours.		
	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.
α......	+14·73°	+12·78°	+12·17°	+14·34°	+12·47°	+11·86°
$[\alpha]$ ...	350	303	290	341	296	282
[M]...	521	452	431	508	441	420
Rotatory dispersions :	1·210 ; 1·050.			1·209 ; 1·051.		

	Time : 91 hours.			Time : 122 hours.		
α	+14·14°	+12·23°	+11·64°	+14·07°	+12·17	+11·58°
$[\alpha]$ ...	336	290	276	334	289	275
[M]...	501	433	412	498	431	410
Rotatory dispersions :	1·214 ; 1·051.			1·215 ; 1·051.		

The rotatory powers were found to attain constant values after one hundred and twenty-two hours; they do not, however, change continuously with time in one direction, but attain maximum values at about one hundred minutes, and then diminish to the final values attained at one hundred and twenty-two hours. In order to show this, and also the regularity with which the change proceeds, the observed values, α, of the rotatory powers are now stated for the above solution for the mercury green line. At 30 minutes, +14·03°; 32, +14·14°; 34, +14·23°; 36, +14·31°; 38, +14·40°; 40, +14·46°; 42, +14·51°; 44, +14·55°; 45, +14·56°; 55, +14·65°; 70, +14·71°; 100, +14·73°; 190, +14·69°; 6 hours, +14·60°; 23, +14·34°; 51, +14·22°; 91, +14·14°; 122, +14·07°; 240, +14·07°. No trustworthy data could be collected before the first half-hour because that time was necessary for making up the solution, which requires application of heat, and for adjusting it to the standard temperature of 20°.

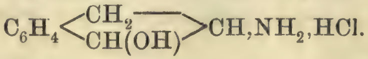
(3) 0·1553 gram in absolute alcohol.

	Time: 30 minutes.			Time: 29 hours.		
	$\mathrm{Hg}_{\text{green}}$.	$\mathrm{Hg}_{\text{yellow}}$.	$\mathrm{Na}_{\text{yellow}}$.	$\mathrm{Hg}_{\text{green}}$.	$\mathrm{Hg}_{\text{yellow}}$.	$\mathrm{Na}_{\text{yellow}}$.
α……	+0·71°	+0·62°	+0·59°	+0·85°	+0·73°	+0·69°
[*α*] …	34·3	29·9	28·5	41·1	35·3	33·3
[M]…	51·1	44·6	42·5	61·2	52·6	49·7
Rotatory dispersions:	1·203; 1·051.			1·232; 1·058.		

	Time: 50 hours.			Time: 104 hours.		
α……	+0·91°	+0·79°	+0·75°	+0·98°	+0·85°	+0·81°
[*α*] …	44·0	38·2	36·2	47·3	41·1	39·1
[M]…	65·5	56·9	54·0	70·6	61·2	58·3
Rotatory dispersions:	1·213; 1·053.			1·210; 1·049.		

The extent of the mutarotation is much greater in alcoholic than in acetone solutions, and its direction is in the opposite sense. It will be seen that the concentration of the solution exerts an influence both on the velocity of the mutarotation and the extent to which it proceeds.

d(or l)-*Hydroxyhydrindamine Hydrochloride*,



$$C_6H_4<\begin{matrix}CH_2\\CH(OH)\end{matrix}>CH,NH_2,HCl.$$

The optically active hydrochlorides are precipitated from the acetone solution of the base by addition of hydrochloric acid; they crystallise from aqueous acetone in long, colourless needles, which are highly lustrous, and are less soluble than the externally compensated salt:

0·2586 required 13·9 c.c. N/10-$AgNO_3$. Cl = 19·06.

$C_9H_{11}ON,HCl$ requires Cl = 19·11 per cent.

The following determinations of rotatory power may be quoted:

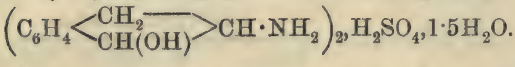
	0·0940 gram *d*-hydrochloride in H_2O.			0·0862 gram *l*-hydrochloride in H_2O.		
	$\mathrm{Hg}_{\text{green}}$.	$\mathrm{Hg}_{\text{yellow}}$.	$\mathrm{Na}_{\text{yellow}}$.	$\mathrm{Hg}_{\text{green}}$.	$\mathrm{Hg}_{\text{yellow}}$.	$\mathrm{Na}_{\text{yellow}}$.
α……	+0·49°	+0·43°	+0·41°	−0·45°	−0·39°	−0·38°
[*α*] …	39·1	34·3	32·7	39·2	33·9	33·1
[M]…	72·5	63·7	60·7	72·7	63·0	61·4
Rotatory dispersions:	1·195; 1·049.			1·184; 1·026.		

	0·1927 gram *d*-hydrochloride in H_2O.			0·1818 gram *l*-hydrochloride in H_2O.		
α……	+1·00°	+0·87°	+0·83°	−0·94°	−0·82°	−0·78°
[*α*] …	38·9	33·9	32·3	38·8	33·8	32·2
[M]…	72·2	62·8	60·0	72·0	62·8	59·7
Rotatory dispersions:	1·205; 1·048.			1·205; 1·051.		

The mean molecular rotatory powers for the basic ion are thus: $[M]_{\mathrm{Hg\ green}} \pm 72·4°$; $[M]_{\mathrm{Hg\ yellow}} \pm 63·1°$; $[M]_{\mathrm{Na\ yellow}} \pm 60·5°$.

Owing to the sparing solubility of these salts in organic solvents, their rotation constants were only determined in aqueous solutions.

d(or l)-*Hydroxyhydrindamine Sulphate*,



$$\left(C_6H_4{<}\begin{matrix}CH_2\\CH(OH)\end{matrix}{>}CH\cdot NH_2\right)_2,H_2SO_4,1\cdot5H_2O.$$

These salts are readily obtained by the addition of sulphuric acid to solutions of the corresponding bases in acetone; they are crystalised from aqueous acetone, and are readily soluble in water, from which they crystallise in long, lustrous needles. They differ from the externally compensated salt in being much more soluble and in retaining water of crystallisation:

0·3877 gave 0·2110 $BaSO_4$. $SO_4 = 22·86$.
0·8979 lost 0·0582 at 100°. $H_2O = 6·48$.
$(C_9H_{11}ON)_2,H_2SO_4,1·5H_2O$ requires $SO_4 = 22·70$;
$H_2O = 6·38$ per cent.

The following determinations of rotatory power were made with the anhydrous salt:

	0·1184 gram in water.			0·2208 gram in water.		
	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α......	+0·57°	+0·50°	+0·47°	+1·05°	+0·92°	+0·87°
[α] ...	36·1	31·7	29·8	35·7	31·3	29·6
[M]...	71·5	62·8	60·0	70·7	61·9	58·6
Rotatory dispersions:	1·213 ; 1·064.			1·207 ; 1·057.		

	0·4035 gram in water.			0·1033 gram in 70 per cent. acetone.		
α......	+1·90°	+1·65°	+1·57°	+0·56°	+0·48°	+0·46°
[α] ...	35·3	30·7	29·2	40·7	34·9	33·4
[M]...	70·0	60·8	57·8	80·6	69·1	66·2
Rotatory dispersions:	1·210 ; 1·051.			1·217 ; 1·044.		

No mutarotation was observed with the aqueous solutions, but in the dilute acetone the rotatory powers diminished by 2 to 3 per cent. in seventeen hours. The diminution in rotatory power with increase of concentration is slight, but rather more distinct than in the case of the hydrochloride.

d(or l)-*Hydroxyhydrindamine Nitrate*, $C_9H_9O\cdot NH_2,HNO_3$.

The optically active nitrates are most readily prepared by treating solutions of the corresponding hydrochlorides with the requisite quantity of silver nitrate solution; the salts separate from a mixture of acetone and ethyl acetate in long, silky needles. They are very soluble in water, and, although practically insoluble in acetone, dissolve readily in this solvent on the addition of a little water:

0·2186 gave 0·4070 CO_2 and 0·1115 H_2O. $C = 50·78$; $H = 5·71$.
$C_9H_{11}ON,HNO_3$ requires $C = 50·92$; $H = 5·70$ per cent.

The following determinations of rotatory power were made with *l*-hydroxyhydrindamine nitrate:

0·2155 gram in water.

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α	−0·97°	−0·84°	−0·80°
[α]	33·8	29·2	27·8
[M]	71·6	62·0	59·1

Rotatory dispersions: 1·213; 1·050.

It is obvious from the identity of the above molecular rotatory powers with those obtained for the hydrochloride and the sulphate in aqueous solution that the nitrate also gives normal values for its rotation constants.

0·1023 gram in 98 per cent. acetone.

Time: 30 minutes.

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α	−1·02°	−0·88°	−0·81°
[α]	74·8	64·5	59·4
[M]	159	137	126

Rotatory dispersions: 1·259; 1·086.

Time: 19 hours.

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α	−0·89°	−0·77°	−0·71°
[α]	65·3	56·5	52·1
[M]	138	120	110

1·254; 1·085.

The mutarotation is much greater in acetone solution for the nitrate than for the sulphate; this is very probably due to it having been possible to dissolve the nitrate with the aid of less water than in the case of the sulphate.

d-*Hydroxyhydrindamine* d-*Camphor-β-sulphonate*, $C_9H_9O\cdot NH_2,C_{10}H_{15}O\cdot SO_3H$.

This salt is obtained by evaporating an acetone solution of equivalent quantities of the base and acid and adding ethyl acetate; it crystallises in small, colourless needles, which decompose at about 260°, and is very soluble in alcohol or water:

0·1293 gave 0·2845 CO_2 and 0·0825 H_2O. C = 60·01; H = 7·14.

$C_9H_{11}ON,C_{10}H_{16}O_4S$ requires C = 59·80; H = 7·14 per cent.

The following determinations of rotatory power were made:

0·2106 gram in water.

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α	+1·07°	+0·92°	+0·88°
[α]	38·1	32·8	31·3
[M]	145	125	120

Rotatory dispersions: 1·216; 1·045.

0·4147 gram in water.

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α	+2·13°	+1·83°	+1·75°
[α]	38·5	33·1	31·7
[M]	147	126	121

1·217; 1·046.

0·2059 gram in acetone.

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α	+2·34°	+2·01°	+1·90°
[α]	85·2	73·2	69·2
[M]	325	279	264

Rotatory dispersions: 1·232; 1·058.

This salt exhibited no mutarotation either in water or pure acetone solutions.

l-*Hydroxyhydrindamine* d-*Camphor-β-sulphonate.*

The above salt, prepared in a similar manner to the previous one, resembles the latter in appearance, and is more soluble in water and acetone; it melts at 192°:

0·2110 gave 0·4605 CO_2 and 0·1335 H_2O. C = 59·52; H = 7·08.

$C_9H_{11}ON,C_{10}H_{16}O_4S$ requires C = 59·80; H = 7·14 per cent.

The following determinations of rotatory power were made:

	0·3890 gram in water.			0·6814 gram in water.		
	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.
α......	−0·09°	−0·13°	−0·13°	−0·14°	−0·22°	−0·23°
[α] ...	1·7	2·5	2·5	1·5	2·4	2·5
[M]...	6·6	9·6	9·6	5·9	9·2	9·7
Rotatory dispersions:	0·69 ; 1·00.			0·51 ; 0·96.		

The algebraic difference of the molecular rotatory powers of these two salts, *dBdA* and *lBdA*, in aqueous solution should be equal to twice the molecular rotatory power of the acid ion; the algebraic sum should be twice the value of [M] for the basic ion. Taking the mean values of [M] for the two salts respectively as +146°, +125·5°, and +120·5°, and −6·3°, −9·4°, and −9·7° for the three wave-lengths respectively, the corresponding values for the acid are calculated as +69·9°, +58·1°, and +55·4°, and for the *d*-basic ion, +76·2°, +67·5°, and +65·1°. The values for the acid are appreciably higher than those obtained by Graham for the acid ion (this vol., p. 746); and the values deduced for the basic ion are also higher than those given by the salts with mineral acids in the present paper; this discrepancy is discussed below.

It is very interesting to notice that, owing to the considerable differences between the rotatory dispersions of the acid and basic ion in these salts, *l*-hydroxyhydrindamine *d*-camphor-*β*-sulphonate exhibits anomalous rotatory dispersion; the rotatory powers are less for the mercury green than for the mercury yellow or sodium yellow. The existence of this anomalous dispersion is also suggested in acetone solutions of the salt, as the following numbers indicate:

0·2411 gram in acetone.

	Time: 30 minutes.			Time: 48 hours.		
	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.
α......	−0·23°	−0·21°	−0·21°	−0·20°	−0·18°	−0·17°
[α] ...	7·2	6·5	6·5	6·2	5·6	5·3
[M]...	27·3	24·9	24·9	23·7	21·4	20·2
Rotatory dispersions:	1·095 ; 1·000.			1·176 ; 1·059.		

It is very remarkable that whilst no mutarotation is exhibited by the salt *dAdB*, the closely related salt *dAlB* shows well marked rotatory dispersion.

The Molecular Rotatory Powers of Salts of Optically Active Acids and Bases in Aqueous Solutions.

We are now in possession of very complete data concerning the molecular rotatory powers of the optically active hydroxyhydrindamine salts with the optically active α-bromocamphor-π-sulphonic acids and camphor-β-sulphonic acids; we also know the molecular rotatory powers of *d*(or *l*)-hydroxyhydrindamine hydrochloride, ammonium *d*-α-bromocamphor-π-sulphonate (Pope and Read, Trans., 1910, **97**, 2201), and ammonium *d*-camphor-β-sulphonate (Graham, this vol., p. 746). The quantitative relationship between these sets of values may now be traced, and in the following list the hydroxyhydrindamine ion is referred to as *dB* or *lB*, that of the bromosulphonic acid as *dA* or *lA*, and that of the camphorsulphonic acid in a 1 per cent. aqueous solution as *dA'* or *lA'*. The following observed data may be tabulated:

		$[M]_{\text{Hg green}}$.	$[M]_{\text{Hg yellow}}$.	$[M]_{\text{Na yellow}}$.
1.	*dB*,HCl	+72·4°	+63·1°	+60·5°
2.	*dA*,NH_3	347·0	295·0	279·0
3.	*dA'*,NH_3	66·5	54·1	50·4
4.	*dBdA*	383·0	327·0	307·0
5.	*lBdA*	274·0	232·0	221·0
6.	*dBdA'*	146·0	126·0	121·0
7.	*lBdA'*	−6·3	−9·4	−9·7

Since the above represent molecular rotatory powers of salts which may be regarded as practically completely electrolytically dissociated in the aqueous solutions of the concentrations used, the values 4 to 7 should be obtained by appropriate addition or subtraction of the values 1, 2, and 3. The following values are thus obtained:

		$[M]_{\text{Hg green}}$.	$[M]_{\text{Hg yellow}}$.	$[M]_{\text{Na yellow}}$.
8.	*dBdA*	+419·0	+358·0	+340·0
9.	*lBdA*	275·0	232·0	218·0
10.	*dB'dA'*	139·0	117·0	111·0
11.	*lBdA'*	−5·9	−9·0	10·1

A measure of the agreement is obtained by subtracting the values 4 to 7 from the corresponding values 8 to 11:

8—4.....................	+36·0	+31·0	+33·0
9—5.....................	+ 1·0	0·0	− 3·0
10—6.....................	− 7·0	− 9·0	−10·0
11—7.....................	+ 0·4	+ 0·4	− 0·4

The noteworthy conclusion is thus reached, that whilst the rotatory powers of the salts *lBdA* and *lBdA'* can be calculated with considerable accuracy from the known rotatory powers of the constituent ions, those of the salts in which the ions are of the same sign of rotatory power are entirely abnormal. The same conclusion is indicated by an inspection of the values for the bromocamphorsulphonates of the optically active tetrahydroquinaldines (Pope and Read, Trans., 1910, **97**, 2199), as is shown by the following numbers. This remarkable relationship will be further investigated.

	$[M]_{\text{Hg green}}$.	$[M]_{\text{Hg yellow}}$.	$[M]_{\text{Na yellow}}$.
lBdA observed	+185°	+156°	+147°
,, calculated...............	188	156	145
dBdA observed	489	419	400
,, calculated...............	506	484	413

d-*Hydroxyhydrindamine Carbonate*, $(C_9H_9O{\cdot}NH_2)_2,H_2CO_3$.

The carbonate is precipitated from solution by passing carbon dioxide through a 1 per cent. solution in water of the base; it is not deposited from solutions containing only 0·5 per cent. of the base. It is obtained as a white powder, which melts and blackens at about 150°. As the composition of the salt is of some importance, samples deposited from a strong acetone solution and from a 1 per cent. aqueous solution were analysed with the following results respectively:

0·2155 gave 0·5115 CO_2 and 0·1245 H_2O. C = 64·73; H = 6·46.
0·0775 ,, 0·1805 CO_2 ,, 0·0435 H_2O. C = 63·52; H = 6·28.
$(C_9H_{11}ON)_2,H_2CO_3$ requires C = 63·30; H = 6·72 per cent.

It appears safe to conclude that the pure salt possesses the normal composition, and does not consist of an anhydrocarbonate or a carbamate.

The rotatory powers were determined in aqueous solution, but, since heat has to be applied to effect solution, it is possible that some carbon dioxide was expelled; the numbers obtained for the molecular rotations approximate, however, to those given by other salts with mineral acids:

0·0928 gram in water.

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α	+0·47°	+0·41°	+0·38°
[α]	38·0	33·1	30·7
[M]	68·4	59·7	55·3

Rotatory dispersions: 1·237; 1·079.

The optically active *sulphides* are produced in the same manner as are those of the externally compensated base, but owing to their instability were not further examined.

d-*Hydroxyhydrindamine Platinichloride*, $(C_9H_9O\cdot NH_2)_2,H_2PtCl_6$.

This substance crystallises from hot water in large, diamond-shaped, orange-red plates, which tend to form skeletal growths, and to grow to a large size; it melts at 219°, and is readily soluble in alcohol. The platinichloride of the externally compensated amine melts at 232° (Trans., 1911, **99**, 2079):

0·3616 gave 0·0994 Pt. Pt = 27·49.

$(C_9H_{11}ON)_2,H_2PtCl_6$ requires Pt = 27·56 per cent.

The following determinations of rotatory power were made:

	0·1810 gram in water.			0·3601 gram in water.		
	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.
α......	+0·47°	+0·42°	+0·39°	+0·93°	+0·83°	+0·77°
$[\alpha]$ ...	19·5	17·4	16·2	19·4	17·3	16·0
[M]...	69·0	61·6	57·2	68·6	61·2	56·8
Rotatory dispersions:	1·205; 1·077.			1·208; 1·078.		

The aqueous solutions exhibited no mutarotation.

d-*Hydroxyhydrindamine Picrate*, $C_9H_9O\cdot NH_2,C_6H_2(NO_2)_3\cdot OH$.

The active picrates are much less soluble in acetone than are the optically inactive ones; they crystallise from boiling water, in which they are sparingly soluble, in long, fine, golden-yellow needles, melting at 208°. They are quite different in colour from the inactive picrate (p. 761), which melts at 227°:

0·1495 gave 0·2610 CO_2 and 0·0505 H_2O. C = 47·61; H = 3·78.

$C_9H_{11}ON,C_6H_3O_7N_3$ requires C = 47·60; H = 3·73 per cent.

Owing to the sparing solubility of the salts, no determinations of the rotatory power could be made in aqueous solution, but the following were made in acetone:

0·1297 gram in acetone.

	Time: 30 minutes.			Time: 19 hours.		
	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.
α	0·0°	+0·05°	+0·06°	−0·14°	−0·07°	−0·05°
$[\alpha]$	0·0	2·9	3·5	8·1	4·1	2·9
[M]	0·0	11·0	13·0	31·0	15·0	11·0
Rotatory dispersions:	— ; 0·83.			2·81; 1·40.		

	Time: 43 hours.		
	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.
α	−0·18°	−0·10°	−0·08°
$[\alpha]$	10·4	5·8	4·6
[M]	39·0	22·0	17·0
Rotatory dispersions:	2·25; 1·25.		

The mutarotation exhibited by this salt in acetone is of a very remarkable character. The solution, which is at first slightly dextrorotatory, rapidly acquires a noteworthy lævorotatory power; at the same time the rotatory dispersions change rapidly.

d-*Hydroxyhydrindamine Acetate*, $C_9H_9O\cdot NH_2,C_2H_4O_2$.

Since the salts of the optically active hydroxyhydrindamines appear to exhibit mutarotation in organic solvents, it seemed desirable to collect further data concerning this curious property by the examination of salts of the active bases with organic acids, as these might be expected to dissolve more readily in organic solvents than do the salts with inorganic acids. For this reason the acetate, benzoate, and salicylate were examined. The acetate crystallises from acetone in fine, feathery needles, which melt at about 150° with blackening; it is more sparingly soluble than the corresponding salt of the externally compensated base:

0·1870 gave 0·4336 CO_2 and 0·1205 H_2O. C = 63·24; H = 7·21.

$C_9H_{11}ON,C_2H_4O_2$ requires C = 63·12; H = 7·23 per cent.

The following determinations of rotatory power were made:

	0·1008 gram in water.			0·2046 gram in water.		
	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.
α......	+0·46°	+0·40°	+0·38°	+0·94°	+0·82°	+0·77°
[α] ...	34·2	29·8	28·3	34·5	30·1	28·2
[M]...	71·6	62·2	59·1	72·1	62·9	59·0
Rotatory dispersions : 1·211 ; 1·053.				1·221 ; 1·065.		

No mutarotation was observed in the aqueous solutions.

0·2069 gram in acetone.

	Time : 30 minutes.			Time : 18 hours.		
α......	+6·56°	+5·70°	+5·45°	+6·22°	+5·41°	+5·15°
[α] ...	238	207	198	226	196	187
[M]..	497	432	413	472	410	390
Rotatory dispersions : 1·204 ; 1·046.				1·208 ; 1·050		

	Time : 40 hours.			Time : 96 hours.		
α......	+5·94°	+5·15°	+4·92°	+5·60°	+4·88°	+4·66°
[α] ...	215	187	178	203	177	169
[M]...	450	390	373	425	370	353
Rotatory dispersions : 1·207 ; 1·047.				1·202 ; 1·047.		

The rotatory powers in acetone are seen to be about seven times as great as those in water; the mutarotation is very strongly marked.

1-*Hydroxyhydrindamine Benzoate*, $C_9H_9O \cdot NH_2,C_7H_6O_2$.

This salt crystallises from acetone in small, light needles, which melt at about 185° with blackening; it is less soluble than the corresponding externally compensated salt:

0·1214 gave 0·3140 CO_2 and 0·0700 H_2O. C=70·54; H=6·45.

$C_9H_{11}ON,C_7H_6O_2$ requires C=70·81; H=6·32 per cent.

The following determinations of rotatory power were made:

0·1420 gram in water.

	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.
α	−0·51°	−0·44°	−0·42°
[α]	26·9	23·2	22·2
[M]	73·0	63·0	60·0

Rotatory dispersions: 1·214; 1·048.

0·1459 gram in acetone.

Time: 30 minutes.

	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.
α......	−3·37°	−2·93°	−2·77°
[α] ...	173	150	142
[M]...	470	407	386

Rotatory dispersions: 1·217; 1·057.

Time: 48 hours.

	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.
α	−3·00°	−2·61°	−2·46°
[α]	154	134	127
[M]	418	364	343

1·220; 1·061.

Time: 60 hours.

α......	−2·92°	−2·52°	−2·40°
[α] ...	150	130	123
[M]...	407	351	335

Rotatory dispersions: 1·217; 1·050.

Time: 107 hours.

α	−2·88°	−2·49°	−2·37°
[α]	148	128	122
[M]	401	347	330

1·215; 1·051.

Again, the rotation constants are much higher in acetone than in water, and very marked mutarotation is exhibited by the acetone solutions.

1-*Hydroxyhydrindamine Salicylate*, $C_9H_9O \cdot NH_2,C_7H_6O_3$.

This salt resembles the inactive isomeride, and is similarly prepared; it melts sharply at 166—167°:

0·1268 gave 0·3100 CO_2 and 0·0685 H_2O. C=66·68; H=6·05.

$C_9H_{11}ON,C_7H_6O_3$ requires C=66·86; H=5·97 per cent.

The following determinations of rotatory power were made:

0·1747 gram in acetone.

0·1365 gram in water.

	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.
α......	−0·46°	−0·40°	−0·38°
[α] ...	25·3	22·0	21·4
[M]...	73	63	60

Rotatory dispersions: 1·211; 1·053.

Time: 30 minutes.

	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.
α	−1·72°	−1·48°	−1·42°
[α]	73·8	63·5	61·0
[M]	212	182	175

1·211; 1·042.

0·1747 gram in acetone (*continued*).

Time : 19 hours.

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α……	−1·34°	−1·15°	−1·08°
[α] …	57·5	49·4	46·4
[M]…	165	142	133

Rotatory dispersions : 1·241 ; 1·065.

Time : 67 hours.

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α	−0·91°	−0·78°	−0·73°
[α]	39·1	33·5	31·3
[M]	112	96	90

1·233 ; 1·068.

Time : 91 hours.

α……	−0·82°	−0·71°	−0·67°
[α] …	35·2	30·5	28·8
[M]…	101	88	83

Rotatory dispersions : 1·224 ; 1·058.

Time : 136 hours.

α	−0·78°	−0·67°	−0·64°
[α]	33·5	28·8	27·5
[M]	96	83	79

1·219 ; 1·047.

Time : 263 hours.

α……	−0·91°	−0·78°	−0·73°
[α] …	39·1	33·5	31·3
[M] ..	112	96	90

Rotatory dispersions : 1·233 ; 1·068.

Time : 378 hours.

α	−0·93°	−0·80°	−0·74°
[α]	39·9	34·3	31·8
[M]	115	99	91

1·257 ; 1·081.

Thus a close similarity exists between the free base and the acetate, benzoate, and salicylate, both as regards the high values of the rotation constants in acetone solution and the considerable range of the mutarotation.

l-1-*Hydroxy-2-benzoylhydrindamide*, $C_9H_9O\cdot NH\cdot CO\cdot C_6H_5$.

The active benzoyl derivative, prepared by the Schotten-Baumann reaction, crystallises from boiling alcohol in soft, silky needles melting at 228°; it is sparingly soluble in organic solvents, the best solvent being acetone, of which 100 c.c. dissolves about 0·3 gram of the substance at the ordinary temperature:

0·2662 gave 0·7370 CO_2 and 0·1445 H_2O. C = 75·51 ; H = 6·07.
$C_{16}H_{15}O_2N$ requires C = 75·85 ; H = 5·97 per cent.

d-1-*Hydroxy-2-benzylidenehydrindamine*, $C_9H_9O\cdot N{:}CH\cdot C_6H_5$.

This substance is prepared in the same manner as its optically inactive isomeride, and is sparingly soluble in hot acetone, from which it crystallises in short, transparent prisms melting at 188°; it is moderately soluble in alcohol:

0·1560 gave 0·4650 CO_2 and 0·0885 H_2O. C = 81·29 ; H = 6·35.
$C_{16}H_{15}ON$ requires C = 80·97 ; H = 6·38 per cent.

The following determinations of the rotation constants of the above two substances were made:

l-1-*Hydroxy-2-benzoylhydrindamide.*

0·0774 gram in acetone.

	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.
α......	−0·71°	−0·62°	−0·60°
[α]...	68·8	60·1	58·1
[M]..	174	152	147

Rotatory dispersions: 1·183; 1·033.

d-1-*Hydroxy-2-benzylidenehydrindamine.*

0·1066 gram in alcohol.

	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.
α......	+1·57°	+1·36°	+1·28°
[α]...	111·0	95·7	90·1
[M]..	262	227	214

1·227; 1·063.

The rotatory powers of the above two substances are of the same sign as those of the bases from which they are prepared.

d-1-*Hydroxy-2-carbamidohydrindene*, $C_9H_9O\cdot NH\cdot CO\cdot NH_2$.

This substance resembles the externally compensated derivative, and melts at 245°:

0·2190 gave 0·4980 CO_2 and 0·1275 H_2O. $C = 62·02$; $H = 6·51$.

$C_{10}H_{12}O_2N_2$ requires $C = 62·46$; $H = 6·30$ per cent.

Owing to its sparing solubility in the ordinary solvents, the rotation constants were determined in acid solutions:

0·1159 gram in acetic acid.

	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.
α......	−0·07°	−0·07°	−0·07°
[α]...	4·5	4·5	4·5
[M]...	8·7	8·7	8·7

Rotatory dispersions: 1·00; 1·00.

0·1266 gram in concentrated hydrochloric acid.

	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.
α......	+1·21°	+1·04°	+1·00°
[α]...	71·7	61·6	59·2
[M]...	138	118	114

1·210; 1·040.

It is interesting to observe that the rotatory powers of the carbamide are of opposite sign in glacial acetic acid and concentrated hydrochloric acid solution. Neither of the three substances last described exhibits mutarotation.

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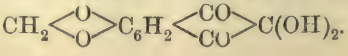
LXXXII.—*Triketomethylenedioxyhydrindene.*

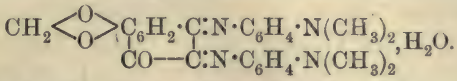
By SIEGFRIED RUHEMANN.

THE experiments recorded in this paper were undertaken with the object of producing an analogue of triketohydrindene hydrate which can be isolated more readily than this compound, and which gives a similar colour-reaction with proteins and their hydrolytic products. This task has been accomplished by the preparation of triketo-5:6-methylenedioxyhydrindene hydrate,



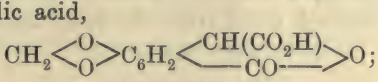
$$CH_2{<}^{O}_{O}{>}C_6H_2{<}^{CO}_{CO}{>}C(OH)_2.$$

This substance is formed from 5:6-methylenedioxy-1-hydrindone in the same way as triketohydrindene hydrate (Trans., 1910, **97**, 1438), namely, by the action of *p*-nitrosodimethylaniline and subsequent treatment of the green condensation product,



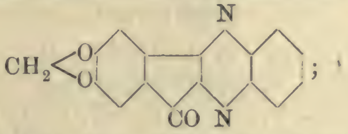
$$CH_2{<}^{O}_{O}{>}\begin{array}{l}C_6H_2\cdot C{:}N\cdot C_6H_4\cdot N(CH_3)_2\\ \;\;CO{-}{-}C{:}N\cdot C_6H_4\cdot N(CH_3)_2\end{array},H_2O.$$

which is formed with dilute mineral acids. The isolation of the triketohydrindene hydrate does not present any difficulty, because it is far less soluble in water or alcohol than the parent substance. In its chemical behaviour it closely resembles it; potassium hydroxide transforms the compound $C_{10}H_6O_6$ into methylenedioxyphthalidecarboxylic acid,

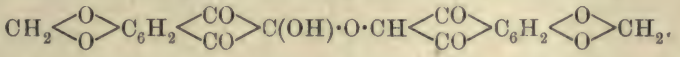


$$CH_2{<}^{O}_{O}{>}C_6H_2{<}^{CH(CO_2H)}_{CO}{>}O;$$

with guanidine or benzamidine it forms colourless additive products; with *o*-phenylenediamine it condenses to the phenazine,

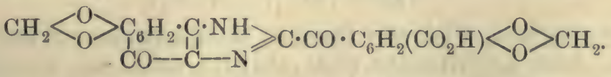


and on reduction it yields bismethylenedioxyhydrindantin,



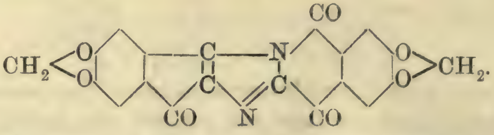
$$CH_2{<}^{O}_{O}{>}C_6H_2{<}^{CO}_{CO}{>}C(OH)\cdot O\cdot CH{<}^{CO}_{CO}{>}C_6H_2{<}^{O}_{O}{>}CH_2.$$

The latter substance, which is conveniently prepared by using dialuric acid as a reducing agent, dissolves in hot sodium carbonate to form a deep red solution, whereas its solution in potassium hydroxide is blue. This behaviour agrees with the property of hydrindantin (Trans., 1911, **99**, 792). Triketomethylenedioxyhydrindene hydrate, as well as the corresponding derivative of hydrindantin, gives deep blue colorations with proteins and their hydrolytic products, although this reaction does not take place so readily as with the parent substances. The triketone hydrate, $C_{10}H_6O_6$, also dissolves in ammonia to yield a reddish-violet solution, from which a red solid is precipitated on the addition of hydrochloric acid. In the light of the view expressed before (Trans., 1910, **97**, 1441) concerning the nature of the compound which is formed from triketohydrindene hydrate on treatment with ammonia, this product is probably to be represented thus:



$$CH_2{<}^{O}_{O}{>}\begin{array}{l}C_6H_2\cdot C\cdot NH\\ \;\;CO{-}{-}C{-}{-}N\end{array}{\geqslant}C\cdot CO\cdot C_6H_2(CO_2H){<}^{O}_{O}{>}CH_2.$$

It dissolves in a large volume of boiling glacial acetic acid, but the dark red substance which separates on cooling is no longer soluble in ammonia or alkalis. The analytical results point to the formula $C_{20}H_8O_7N_2$ for the compound, and indicate that, in the process of crystallisation, the first-formed substance loses 1 molecule of water to form the condensation product:



Triketomethylenedioxyhydrindene hydrate differs from its parent substance inasmuch as it yields a monophenylhydrazone and a monosemicarbazone, as compared with the dihydrazone and disemicarbazone which are formed from triketohydrindene hydrate.

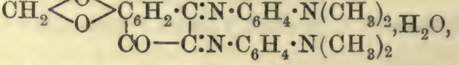
EXPERIMENTAL.

Action of p-*Nitrosodimethylaniline on* 5:6-*Methylenedioxy-1-hydrindone.*

The hydrindone which was obtained by the action of phosphoric oxide on the solution of piperonylpropionic acid in benzene (see Perkin and Robinson, Trans., 1907, **95**, 1084) is only moderately soluble in ether or hot alcohol, but more readily so in chloroform. It condenses with *p*-nitrosodimethylaniline under the same conditions as α-hydrindone, namely, by mixing it (4 grams) with the base (14 grams), dissolved in boiling alcohol, and gradually adding a small quantity of alcoholic potassium hydroxide to the solution, which is previously cooled to the temperature of the room. The mixture turns deep brown, and in a short time deposits beautiful, green crystals; the reaction is complete after two to three hours. The solid (7·2 grams) is washed with cold alcohol, and, for analysis, purified by dissolving it in boiling chloroform and adding alcohol to the hot solution, when, on cooling, green prisms separate which melt and decompose at 194—195°:

0·2035 * gave 0·5080 CO_2 and 0·1045 H_2O. C=68·08; H=5·70.
0·2045 „ 21·8 c.c. N_2 at 20° and 762 mm. N=12·22.
$C_{26}H_{26}O_4N_4$ requires C=68·12; H=5·67; N=12·23 per cent.

The analytical results point to the formula:



$$CH_2{<}^{O}_{O}{>}\begin{array}{l}C_6H_2\cdot C{:}N\cdot C_6H_4\cdot N(CH_3)_2\\ CO-C{:}N\cdot C_6H_4\cdot N(CH_3)_2\end{array},H_2O,$$

which corresponds with the formula of the compound previously obtained from α-hydrindone (*loc. cit.*); the substance, accordingly, is to be regarded as the *hydrate* of 2:3-*bis*(p-*dimethylaminoanilo*)-

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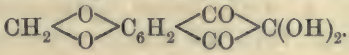
* Dried at 100°.

5:6-*methylenedioxy*-1-*hydrindone.* It is only sparingly soluble in boiling alcohol, yielding a bluish-black solution; more readily it dissolves in hot chloroform.

The dark alcoholic mother liquor of the product of the reaction between nitrosodimethylaniline and methylenedioxyhydrindone, when kept for several days at the ordinary temperature, deposits a brown solid, which is sparingly soluble in alcohol, readily, however, in boiling benzene, and on cooling crystallises in red needles which possess a blue lustre and melt at 262°. These properties, together with the analysis (Found, C = 71·68; H = 7·40. Calc., C = 71·64; H = 7·46 per cent.), characterise the compound as tetramethyldiaminoazobenzene, $(CH_3)_2N{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}N(CH_3)_2$, which, no doubt, owes its formation to the reduction of nitrosodimethylaniline by the alcoholic potassium hydroxide.

Triketo-5:6-*methylenedioxyhydrindene Hydrate,*



$$CH_2{<}\genfrac{}{}{0pt}{}{O}{O}{>}C_6H_2{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}C(OH)_2.$$

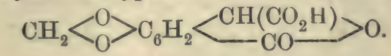
The green bisazomethine, $C_{26}H_{26}O_4N_4$, has basic properties; on the addition of cold dilute sulphuric acid, it turns red and forms a sulphate, which, however, is unstable, and readily dissociates when washed with water. If, on the other hand, the substance is digested with the acid on the water-bath, the red salt which is first produced decomposes, yielding a dark liquid and a brown solid. This is washed with cold water, then dissolved in hot water, and the solution boiled with animal charcoal. The filtrate, on cooling, deposits light yellow prisms, which, on heating, turn red, and melt and decompose at 236°. The compound, after drying in the water-oven, gave the following results:

0·2100 gave 0·4165 CO_2 and 0·0520 H_2O. C = 54·09; H = 2·75.

$C_{10}H_6O_6$ requires C = 54·05; H = 2·70 per cent.

Triketomethylenedioxyhydrindene hydrate is sparingly soluble in cold, moderately so in boiling water, and with amino-acids gives a deep blue colour-reaction, which, however, occurs less readily, as in the case of triketohydrindene hydrate.

Methylenedioxyphthalidecarboxylic Acid,



$$CH_2{<}\genfrac{}{}{0pt}{}{O}{O}{>}C_6H_2{<}\genfrac{}{}{0pt}{}{CH(CO_2H)}{—CO—}{>}O.$$

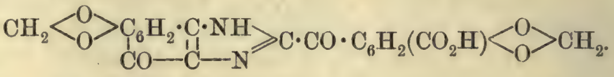
Triketomethylenedioxyhydrindene hydrate, on warming with dilute potassium hydroxide, turns yellowish-red, and then dissolves to yield a deep reddish-violet solution, which subsequently becomes lighter in colour, and finally colourless on the addition of dilute sulphuric acid. If the acid liquor is digested on the water-bath for about an hour, it deposits a colourless solid, which is soluble in boiling water, and on cooling crystallises in prisms, which melt and evolve carbon dioxide at 216°:

0·2057 gave 0·4077 CO_2 and 0·0520 H_2O. C = 54·04; H = 2·80.
$C_{10}H_6O_6$ requires C = 54·05; H = 2·70 per cent.

Methylenedioxyphthalidecarboxylic acid is sparingly soluble in cold, moderately so in boiling, water or in ether, but readily so in hot alcohol.

Action of Ammonia on Triketomethylenedioxyhydrindene Hydrate.

The triketone dissolves in dilute ammonia, gradually at the ordinary temperature, more readily on warming, to form a deep reddish-violet solution, which, on the addition of dilute hydrochloric acid, yields a dark brown, gelatinous precipitate. As pointed out before (p. 781), the substance probably is to be represented thus:

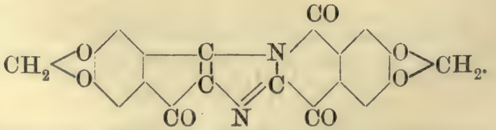


$$CH_2{<}^{O}_{O}{>}\underset{CO\text{---}C\text{---}N}{C_6H_2\cdot C\cdot NH}{\geqslant}C\cdot CO\cdot C_6H_2(CO_2H){<}^{O}_{O}{>}CH_2.$$

It is readily soluble in ammonia or potassium hydroxide, and the solution in ammonia gives a dark brown silver salt on treatment with silver nitrate. The condensation product is insoluble in alcohol or chloroform, but dissolves in a large volume of boiling glacial acetic acid, and on cooling dark red prisms gradually separate, which do not melt at 360°:

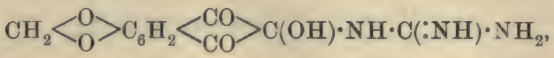
0·2107 gave 0·4780 CO_2 and 0·0410 H_2O. C = 61·87; H = 2·16.
0·2200 „ 14 c.c. N_2 at 18° and 760 mm. N = 7·34.
$C_{20}H_8O_7N_2$ requires C = 61·86; H = 2·06; N = 7·22 per cent.

This compound is insoluble in alkalis, and this fact, together with the analytical results, indicate that the direct product of the reaction between the triketone and ammonia, on boiling with glacial acetic acid, has lost 1 molecule of water and condensed to the cyclic system:



Additive Products of Triketomethylenedioxyhydrindene Hydrate with Guanidine and Benzamidine.

These substances are obtained in the same way as the corresponding compounds from triketohydrindene hydrate (Trans., 1910, **97**, 2025). The *product*,

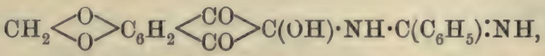


$$\mathrm{CH_2<\substack{O\\O}>C_6H_2<\substack{CO\\CO}>C(OH)\cdot NH\cdot C(:NH)\cdot NH_2},$$

which is formed by the action of guanidine on the hot aqueous solution of the triketone hydrate, $C_{10}H_6O_6$, separates in colourless needles; on heating, it gradually turns black, but does not melt at 300°:

0·2095 gave 0·3845 CO_2 and 0·0650 H_2O. C=50·05; H=3·44.
0·1955 „ 27·2 c.c. N_2 at 190° and 764 mm. N=16·08.
$C_{11}H_9O_3N_3$ requires C=50·19; H=3·42; N=16·0 per cent.

The *additive product*,

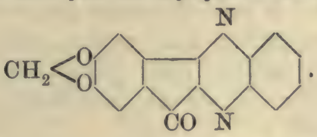


$$\mathrm{CH_2<\substack{O\\O}>C_6H_2<\substack{CO\\CO}>C(OH)\cdot NH\cdot C(C_6H_5):NH},$$

of the triketone with benzamidine separates from the hot aqueous solution of the mixture of triketomethylenedioxyhydrindene hydrate, benzamidine hydrochloride, and sodium carbonate in colourless plates, which darken at about 220° and melt at 239—240° with evolution of gas:

0·2165 gave 16·8 c.c. N_2 at 23° and 765 mm. N=8·80.
$C_{17}H_{12}O_5N_2$ requires N=8·64 per cent.

1-*Keto*-5:6-*methylenedioxyhydrindenophenazine*,



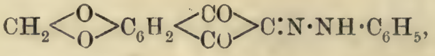
This compound is precipitated as a red solid on mixing the hot aqueous solution of the hydrate, $C_{10}H_6O_6$, with *o*-phenylenediamine dissolved in dilute acetic acid. It is insoluble in cold, sparingly soluble in hot, alcohol, more readily so in boiling glacial acetic acid, and on cooling crystallises from this solution in red prisms, which melt at 290° after having turned brown a few degrees before:

0·2082 gave 0·5315 CO_2 and 0·0565 H_2O. C=69·62; H=3·02.
0·2102 „ 19·2 c.c. N_2 at 21° and 755 mm. N=10·32.
$C_{16}H_8O_3N_2$ requires C=69·57; H=2·90; N=10·14 per cent.

The Phenylhydrazone and Semicarbazone of Triketomethylenedioxyhydrindene.

As stated before (p. 782), the triketone reacts only with 1 molecule of phenylhydrazine or semicarbazide.

The *phenylhydrazone*,

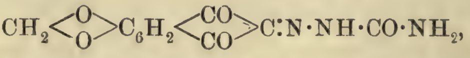


$$\mathrm{CH_2{<}\substack{O\\O}{>}C_6H_2{<}\substack{CO\\CO}{>}C{:}N{\cdot}NH{\cdot}C_6H_5},$$

is precipitated on mixing the solution of the hydrate, $C_{10}H_6O_6$, with phenylhydrazine dissolved in acetic acid. It is sparingly soluble in alcohol, but dissolves more readily in boiling glacial acetic acid, and on cooling crystallises in clusters of orange needles, which melt and decompose at 265°:

0·2070 gave 0·4960 CO_2 and 0·0630 H_2O. $C=65·34$; $H=3·38$.
0·2025 „ 16·8 c.c. N_2 at 15° and 755 mm. $N=9·65$.
$C_{16}H_{10}O_4N_2$ requires $C=65·31$; $H=3·40$; $N=9·52$ per cent.

The *semicarbazone*,

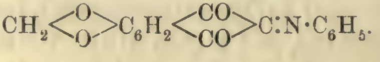


$$\mathrm{CH_2{<}\substack{O\\O}{>}C_6H_2{<}\substack{CO\\CO}{>}C{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2},$$

is characterised by its brick-red colour. This property, which appears to be without analogy, is the more surprising since the phenylhydrazone, described above, as well as the disemicarbazone of triketohydrindene (Trans., 1910, **97**, 1448), are much lighter in colour. I am, as yet, unable to account for this remarkable phenomenon. The semicarbazone is formed by dissolving triketomethylenedioxyhydrindene hydrate (1 gram) in hot water (about 150 c.c.), then cooling the solution to the temperature of the room, and adding an excess of semicarbazide oxalate (3 grams) dissolved in water. A red coloration soon occurs, and a solid gradually separates, which crystallises from glacial acetic acid in minute, brick-red plates; they are almost insoluble in alcohol, and melt and decompose at 266°:

0·2053 gave 0·3770 CO_2 and 0·0510 H_2O. $C=50·53$; $H=2·76$.
0·1909 „ 27·4 c.c. N_2 at 19° and 745 mm. $N=16·16$.
$C_{11}H_7O_5N_3$ requires $C=50·57$; $H=2·68$; $N=16·09$ per cent.

1 : 3-*Diketo*-5 : 6-*methylenedioxyhydrindylideneaniline*,

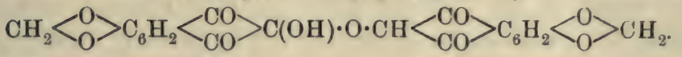


$$\mathrm{CH_2{<}\substack{O\\O}{>}C_6H_2{<}\substack{CO\\CO}{>}C{:}N{\cdot}C_6H_5}.$$

On shaking the cold aqueous solution of the triketone hydrate, $C_{10}H_6O_6$, with aniline, a yellow, crystalline solid is formed similar to the substance which is produced from triketohydrindene hydrate (Trans., 1910, **97**, 1447). This compound is also unstable, and is decomposed by hot water with separation of aniline; for analysis it was washed with water, then with ether, in which it is not readily soluble, and dried in a vacuum desiccator over sulphuric acid, when it turns yellowish-red; it reddens at 110°, and melts and decomposes at 117°:

0·2200 gave 10·4 c.c. N_2 at 20° and 747 mm. $N=5·31$.
$C_{16}H_9O_4N$ requires $N=5·02$ per cent.

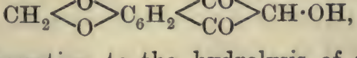
Bismethylenedioxyhydrindantin,


$$CH_2{<}\substack{O\\O}{>}C_6H_2{<}\substack{CO\\CO}{>}C(OH)\cdot O\cdot CH{<}\substack{CO\\CO}{>}C_6H_2{<}\substack{O\\O}{>}CH_2.$$

The triketone, $C_{10}H_6O_6$, is reduced by hydrogen sulphide as readily as the parent substance (Trans., 1911, **99**, 792), and yields a white solid, which undoubtedly contains the derivative of hydrindantin besides sulphur, but a separation cannot be effected owing to the fact that the substituted hydrindantin is only sparingly soluble in water or organic solvents. The compound, however, can be prepared with the greatest ease by making use of the observation that triketohydrindene hydrate is readily reduced to hydrindantin by dialuric acid (Trans., 1911, **99**, 1306). On boiling for a short time the mixture of equal weights (1 gram) of the triketone, $C_{10}H_6O_6$, and dialuric acid dissolved in water, the derivative of hydrindantin separates in faintly-coloured plates, which, after washing with warm water, are quite pure. This substance, like the parent compound, contains water of crystallisation, which it loses slowly at 100°, but readily at 110°; on heating, it reddens at about 120°, then turns black, and finally melts and evolves gas at 274°:

0·1993 * gave 0·4265 CO_2 and 0·0455 H_2O. $C=58·36$; $H=2·53$.
$C_{20}H_{10}O_{10}$ requires $C=58·54$; $H=2·44$ per cent.

The compound behaves in the same way as hydrindantin (*loc. cit.*); it dissolves in sodium carbonate, as well as in potassium hydroxide, although less readily than the parent substance, and the solution in the carbonate is reddish-violet, whereas the one in the alkali is deep blue. The first undoubtedly contains a salt of the substituted hydrindantin, and the blue coloration of the solution in potassium hydroxide is due to the production of the chromo-salt of hydroxydiketomethylenedioxyhydrindene,


$$CH_2{<}\substack{O\\O}{>}C_6H_2{<}\substack{CO\\CO}{>}CH\cdot OH,$$

which owes its formation to the hydrolysis of the hydrindantin, $C_{20}H_{10}O_{10}$. The latter compound, like the triketone, $C_{10}H_6O_6$, gives the blue colour reaction with amino-acids. This reaction is based on the formation of the analogue of murexide, which is similar to the one previously obtained from triketohydrindene hydrate (Trans., 1911, **99**, 1486). It is formed, although in an impure state, by digesting on the water-bath the aqueous solution of the mixture of equal weights of triketomethylenedioxyhydrindene hydrate and glycine. In a short time a deep blue coloration occurs, simultaneously carbon dioxide is evolved, and finally a bluish-brown solid separates. This product is a mixture, a constituent of which is the analogue of murexide. Attempts to isolate it have not been made on account of its sparing solubility in water.

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* Dried at 110°.

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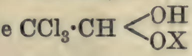
LXXXIII.—*The Action of Chloral on Ethyl Tartrate and on Ethyl Malate.*

By THOMAS STEWART PATTERSON and ANDREW McMILLAN, M.A., D.Sc.

SOME five years ago, while we were engaged in working out a method of following intramolecular change, using an optically active substance as indicator (Trans., 1907, **91**, 504; 1908, **93**, 1041; *Ber.*, 1907, **40**, 2564; *Proc. Roy. Phil. Soc. Glasgow*, 1911, **42**, 10, 26), it occurred to us that it might be possible also to follow, in a somewhat similar fashion, the formation of chloral hydrate from chloral and water, by mixing together chloral, water, and ethyl tartrate, and examining the rotation of the mixture from time to time. The rotation of the ethyl tartrate might be expected to alter as the solvent changed from chloral + water to chloral hydrate. The experiment, although now without theoretical importance, seemed to be worth trying as an example of our method, but we found immediately that ethyl tartrate and chloral combine so rapidly with each other that our original intention could not be realised.

Being, however, considerably impressed by several interesting features in the rotation of chloral solutions of ethyl tartrate, we carried out a number of experiments on the subject. Shortly afterwards there was published a paper by F. Kuntze, working under the direction of J. Gadamer (*Arch. Pharm.*, 1908, **246**, 91), in which, amongst others, chloral *l*-amyl alcoholate was described, and its decomposition in presence of other alcohols followed in the polarimeter. Our collaboration then ceased for a time, but we recently took the subject up again, and were engaged on it when a paper appeared by Grossmann and Landau (*Zeitsch. physikal. Chem.*, 1910, **75**, 129), in which some remarkable results are recorded. These authors have examined the effect on the rotation of ethyl tartrate and ethyl malate, not only of chloral and numerous other solvents, but even of phosphorus trichloride and acetyl chloride as well. In some of these solvents it appears that the rotation altered with time, the phenomenon being referred to as "mutarotation," a peculiarly unfortunate use of the term. In acetyl chloride (*loc. cit.*, p. 184) methyl malate dissolved with such marked heating and evolution of hydrogen chloride that the solution could be introduced into the polarimeter tube only some time after mixing. It then showed no further "mutarotation." The authors cautiously think the "simplest assumption" to make is that acetylation of the hydroxyl group of the ester had occurred, but, they say, "The isolation of the compound formed did not come within the scope of the present research," and thus the rotation of some acetyldimethyl malate, mixed probably with a proportion (unknown) of dimethyl malate, all dissolved in acetyl chloride saturated with hydrogen chloride, is seriously recorded in their tables as the rotation of methyl malate in acetyl chloride. The further investigation of solvents of the type of acetyl chloride and phosphorus trichloride we gladly leave to Grossmann and Landau, but we propose here to describe the results we have obtained in regard to the action of ethyl tartrate and ethyl malate on chloral.

We may first mention that Grossmann and Landau have examined the action of chloral and bromal on ethyl tartrate and ethyl malate. They find in each case that the rotation of the solution rapidly increases with time to reach a maximum, and then falls again to a final value. They think that this "mutarotation" is probably the consequence of a reaction between active substance and solvent (*loc. cit.*, p. 191), "although," they add, "the formation of compounds of the type  $CCl_3{\cdot}CH<^{OH}_{OX}$ as the cause of the mutarotation could not give any explanation of the occurrence of the maximum and the subsequent reversal of rotation."

In table I are recorded the results of our experiments with ethyl tartrate and chloral. Three solutions were examined, the first containing 4 molecules of ethyl tartrate to 1·19 molecules of chloral, the second 1 molecule of ethyl tartrate to 9·91 molecules of chloral, and the third 1 molecule of ethyl tartrate to 22·31 molecules of chloral. It will be observed that the matter is more complex than

TABLE I.

Ethyl Tartrate in Chloral.

I. p* = 82·54.		II. $p = 12·35$.		III. $p = 5·89$.	
T (mins.).	α^{20}_{D} (100 mm.).	T (mins.).	α^{20}_{D} (100 mm.).	T (mins.).	α^{20}_{D} (100 mm.).
0	Ca + 5·0°	0	Ca − 0·3°	0	Ca − 0·1°
30	8·31	2	+ 1·775	7	+ 2·22
55	10·35	7	3·150	12	3·12
135	15·494	10	4·475	25	4·16
170	16·614	13	5·660	40	5·64
200	17·434	19	7·830	70	6·90
265	18·254	25	9·65	100	*7·60*
435	*18·920*	30	10·975	1180	*7·12*
1275	18·714	55	14·795	1420	7·16
(days)		80	16·485		7·30
2	18·460	165	*17·385*		
4	17·944	295	17·035		
6	17·536	1380	15·025		
7	17·504	1695	*14·885*		
11	17·296	2820	15·385		
14	16·912	(days)			
	16·468	4	16·235		
		6	17·125		
			17·126		

* Grams of ethyl tartrate in 100 grams of solution.

Grossmann and Landau state. In the first solution ($p = 82·54$), the observed rotation rises very rapidly from an initial value of *circa* + 5° to reach a maximum of + 18·92° after four hundred and thirty-five minutes. Thereafter, the rotation falls much more slowly, and in the course of about three weeks reaches a final value of + 16·468°.* At the same time the solution becomes very viscid, and a considerable contraction occurs. If, however, the proportion of chloral is higher ($p = 12·35$), the rotation of the mixture again shows a very rapid increase, from about − 0·3° initially to a maximum of + 17·385°, after one hundred and sixty-five minutes, then a more gradual fall to + 14·885°, and thereafter a still slower rise, in the course of about a week, to + 17·126°, a value somewhat lower than the first maximum. When the proportion of chloral is still greater, exactly the same behaviour is observed, except, of course, that the rotational changes are smaller. In a $p = 5·89$ solution a maximum of + 7·6° is reached in one hundred minutes, the minimum is at + 7·12°, whilst the final value is + 7·3°.

Now it has been shown by McCrae and Patterson (Trans., 1900, **77**, 1108) that the substitution of one of the hydroxylic hydrogen atoms of ethyl tartrate by an acyl radicle produces a compound of increased rotation, whereas the substitution of both gives rise to a product of lower rotation than the monoacyl derivative, thus:

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* It may, perhaps, be mentioned that Worley (Trans., 1911, **99**, 351) finds the rotation of a sucrose solution, in presence of an acid, to fall to a minimum and then rise slowly again.

	Diethyl tartrate.	Diethyl mono-monochloroacetyltartrate.	Diethyl di-monochloroacetyltartrate.
M_D^{20} ………	+15·86°	+32·3°	+25·5°

and this has been confirmed by P. F. Frankland, Heathcote, and Miss Hartle (Trans., 1903, **83**, 160) and Frankland, Heathcote, and Green (Trans., 1903, **83**, 170). It seemed possible, therefore, that the chloral first attacks one hydroxyl group, causing a rapid rise of rotation, and then, rather more slowly, the second hydroxyl group, which in accordance with what has just been stated, would probably cause a fall of rotation. The second increase of rotation in the more dilute solutions appeared to indicate that a further reaction occurs, in which one or both of the carbethoxy-groups are concerned.

With a view to determine whether this explanation could be substantiated, we carried out a number of experiments, but before passing on to a description of these we may mention here two points which will call for no further reference.

We tried an experiment in which an indifferent solvent, benzene, was added to the mixture of ethyl tartrate and chloral, with the following results:

TABLE II.

Ethyl Tartrate, Chloral, and Benzene.

	Proportions by weight.	Molecular proportions.
Ethyl tartrate ………………	25·20	1·000
Chloral ………………………	24·99	1·385
Benzene ……………………	49·81	5·22

T (mins.).	α_D^{20} (100 mm.).	T (mins.).	α_D^{20} (100 mm.).
0	+1·15°	535	+4·213°
10	1·259	1385	7·763
25	1·358	1655	8·602
100	1·738	1995	9·506
210	2·373	2915	11·274
320	3·039	4610	12·756
360	3·289	∞	14·005

In this case again the rotation rapidly increased, but no reversal in the direction of the time curve was observed.

We may quote also an experiment made in connexion with our original intention. A solution of ethyl tartrate and chloral hydrate was prepared of much the same concentration as solution I, its rotation being observed from time to time.

Table III.

Ethyl Tartrate in Chloral Hydrate.

p=79·86. (Four molecules of ethyl tartrate to 1·27 molecules of chloral hydrate.)

T.	α_D^{20} (100 mm.).
0 mins.	Ca + 4·5°
45 ,,	5·64
110 ,,	6·82
280 ,,	7·58
1400 ,,	7·85
3 days	7·85

It will be noticed that although reaction occurs, it does not proceed nearly so far nor so quickly as with chloral itself. Starting from an initial value about the same as that for chloral in equivalent concentration, the rotation rises only some 3·35° after fourteen hundred minutes, a less change than occurs in chloral in thirty minutes. There is thus a very marked difference in the reactivity of the two substances, the effect of the reverse reaction due to the influence of the water formed from the chloral hydrate and the ethyl tartrate being very distinct.

With a view to elucidate the reaction between chloral and ethyl tartrate, we next examined that between chloral and ethyl malate, which substance having only one hydroxyl group might be expected to behave differently from ethyl tartrate. The results were as follows:

Table IV.

Ethyl Malate in Chloral.

p=14·81. (Ethyl malate, 1 molecule; Chloral, 7·41 molecules.)

T (mins.).	α_D^{20} (100 mm.).	*T* (mins.).	α_D^{20} (100 mm.).
0	Ca + 1·0°	75	Ca − 14·31°
2	− 1·10	95	15·25
5	1·62	220	*16·35*
10	2·91	1450	15·60
15	4·20	1655	15·45
21	6·33	2880	15·00
35	9·60	4 days	14·13
45	11·40	∞	13·20

The rotation of the solution decreases rapidly from *circa* + 1° initially to reach a minimum of − 16·35° in two hundred and twenty minutes, after which there is a rise, in the course of about a week, of some 3° to the value − 13·2°, the magnitude of the changes being much the same as for ethyl tartrate. The second reversal observed in ethyl tartrate disappears, however, in ethyl malate.

To ascertain if the attainment to a maximum rotation and subsequent diminution is possible for a compound containing only one hydroxyl group and no carbethoxy-groups, we next examined a solution of menthol in chloral, and obtained the following data:

TABLE V.

Menthol in Chloral.

$p=9{\cdot}57$. (Menthol, 1 molecule; Chloral, 10 molecules.)

T (mins.).	α_D^{20} (100 mm.).	*T* (days).	α_D^{20} (100 mm).
0	−19·00°	2	−21·08°
15	19·12	3	21·60
135	19·14	4	22·02
1320	20·24	5	22·30
		7	22·78
		∞	23·02

There was, in the course of a fortnight, a slow change of some 4°, but in one direction only.

We then tried to attack the carbethoxy-groups in a substance not containing free hydroxyl groups, and for this purpose used a solution of diethyl diacetyltartrate and one of diethyl acetylmalate in chloral, the results being as follows:

TABLE VI.

Diethyl Diacetyltartrate in Chloral.

$p=16{\cdot}52$. (Ester, 1 molecule; Chloral, 9·935 molecules.)

T.	α_D^{20} (100 mm.).
0	?
35 mins.	−2·54
1 day	2·58
4 days	2·32
14 ,,	1·80
∞	1·80

TABLE VII.

Diethyl Acetylmalate in Chloral.

$p=15{\cdot}13$. (Ester, 1 molecule; Chloral, 8·83 molecules.)

T.	α_D^{20} (100 mm.).
0	−3·78
5 mins.	3·78
1 day	3·72
2 days	3·69
∞	3·588

In diethyl diacetyltartrate there is a change in the positive direction of about 0·8° and one considerably less in the malate, but these results are not quite conclusive, since it is possible, although not very probable, that chloral could attack the molecule at the oxygen atom joining the CH radicle to the $CH_3{\cdot}CO{\cdot}$ group. We therefore examined the action of chloral on a specimen of dimethyl dimethoxysuccinate, which was kindly supplied to us by Professor J. C. Irvine, to whom we have pleasure in expressing our thanks. The result of the experiment was as follows:

TABLE VIII.

Dimethyl Dimethoxysuccinate in Chloral.

$p=11{\cdot}90$. (Succinate, 1 molecule; Chloral, 10·34 molecules.)

T.	α_D^{20} (100 mm.).
0	+11·90°
4 mins.	11·90
70 ,,	11·90
285 ,,	11·852
1440 ,,	11·56
4 days	11·52
	11·52

There is thus only a slight change of rotation of 0·4°, showing, apparently, that any action there may be on the carbethoxy-groups is very small.

These experiments did not much strengthen the explanation that had suggested itself to us of the rotational changes which occur in chloral solutions of ethyl tartrate, partly because the variations of rotation which could legitimately be attributed to action of chloral on the carbethoxy-groups do not seem to be sufficient to account for the second rise in rotation of dilute solutions of ethyl tartrate in chloral (see table I, solutions II and III), but more especially on account of the fact that ethyl tartrate and ethyl malate as regards the initial rise and subsequent fall behave very much alike. On the hypothesis suggested this would seem to be improbable, since, although the first combination in each case would be similar—action of chloral on an alcoholic hydroxyl group—the second would be quite different—action of chloral on an alcoholic hydroxyl group in the case of the tartrate, and action of chloral on carbethoxy-groups in the case of the malate.

We therefore tried some experiments with the view of isolating the compounds formed in the reaction. No solid separated, on keeping, in any experiments we had made, and to resolve the viscid reaction product into liquid constituents by differential solubility appeared to be hopeless. Therefore, although we scarcely expected that any additive compound formed would survive distillation, we heated a mixture of ethyl tartrate (1 molecule) and chloral (10 molecules) on the water-bath for four hours, distilled off the chloral, and then distilled the very viscid residue under diminished pressure. It passed over at about 200°/14 mm., and had α_D^{15} +35·612°.

This substance yielded chloroform on treatment with sodium hydroxide solution, and on analysis we found Cl = 26·88 per cent. An additive compound of 1 molecule of ethyl tartrate and 1 molecule of chloral would require Cl = 30·21 per cent.

In another experiment we heated 60 grams of ethyl tartrate and 100 grams of chloral in sealed tubes at 130° for twenty-four hours. On distillation, a product boiling at 185—200°/15 mm. was obtained, and after some time this crystallised, yielding a semi-solid mass of fine needles mixed with an oily liquid. The crystals were dried on porous plate, and recrystallised from light petroleum. They melted at 65—67°. On analysis we found Cl = 32·27, and after a further crystallisation, Cl = 34·6 per cent.

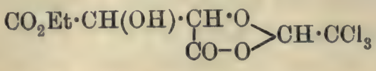
As this lies between the quantity of chlorine required for a compound containing 1 molecule of ethyl tartrate and 1 of chloral and a compound of 1 molecule of ethyl tartrate and 2 molecules of chloral (Cl = 42·52 per cent.), we thought that more vigorous treatment might produce the latter substance, and therefore in our next preparation we heated 50 grams of ethyl tartrate and 120 grams of chloral to 130° for twelve hours. The tube was then opened, the chloral distilled off, 100 grams of fresh chloral added, and the mixture heated again in a sealed tube for eight hours at 160°. This whole process was then repeated with another 100 grams of chloral, heating being continued for six hours at 160° and two hours at 170°. After the chloral had been distilled off as far as possible, the residue gave α_D^{20} + 52·82°. It was then distilled under diminished pressure, and after some time it solidified. It was crystallised from light petroleum, and then gave Cl = 35·42. In methyl-alcoholic solution, 0·2508 gram in 5·2159 grams of solution (c = 4·8 approximately), it had α_D^{26} + 1·22°, whence $[\alpha]_D^{26}$ *ca.* + 25·3°.

This was then recrystallised from light petroleum, when 0·2528 gram in 5·1529 grams of methyl-alcoholic solution (c = 4·9 approximately) gave α_D^{26} + 1·28°, whence $[\alpha]_D^{26}$ + 26°. Analysis of this sample gave Cl = 34·93 and 34·7 per cent. The substance therefore appeared to be homogeneous, and not to be attacked by chloral even after this energetic treatment.

A molecular-weight determination of the compound was next carried out in benzene solution with the following results. K for benzene = 49:

Benzene.	Substance.	*p.*	Depression.	M.W.
17·1169	0·2250	1·31	0·235°	274·3
	0·3455	2 02	0·348	284·3
	0·4436	2·59	0·422	301·1

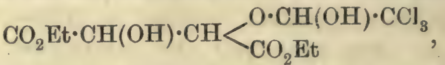
The compound which seems to satisfy the analytical results and also this molecular-weight determination is that represented by the formula:



$$CO_2Et\cdot CH(OH)\cdot\begin{array}{l}CH\cdot O\\ |\\ CO{-}O\end{array}\!\!>CH\cdot CCl_3$$

Cl = 34·6 per cent.; M.W. = 307·5.

It is doubtless formed by combination of chloral with one of the hydroxyl groups of the ethyl tartrate to form the compound:



$$CO_2Et\cdot CH(OH)\cdot CH<\begin{matrix}O\cdot CH(OH)\cdot CCl_3\\ CO_2Et\end{matrix},$$

which then loses a molecule of alcohol. The alcohol liberated would, of course, combine with another molecule of chloral to form chloral alcoholate. We then remembered that in all our preparations there solidified in the condenser a comparatively small quantity of a white substance, which we took to be chloral hydrate. Some of this, which had separated out from the first distillates of a preparation, was then examined. It melted at 57°. Chloral alcoholate melts at 57°, and chloral hydrate at 56°. When mixed with a little chloral alcoholate the melting point remained unaltered, whilst with an approximately equal proportion of chloral hydrate a mixture was obtained melting at *circa* 40°. There was thus no doubt that the substance was chloral alcoholate, which affords important confirmation of the suggestion made above as to the constitution of the product of the reaction between chloral and ethyl tartrate.

We are now in a position to explain, at least partly, the behaviour of chloral solutions of ethyl tartrate and ethyl malate. The initial rise of rotation is due to combination of chloral with a hydroxyl group of the ester molecules; the subsequent fall is due, in both cases, to the elimination of alcohol from one of the carbethoxy-groups. This agrees with the fact that ethyl tartrate and ethyl malate behave, so far, alike; the second rise in the case of ethyl tartrate has to do, doubtless, with the presence of a second hydroxyl group.

The essence of the explanation which we arrive at of the reaction between ethyl tartrate and chloral is the condensation of the primary additive product, and it may very reasonably be objected that this phase of the process might owe its occurrence either to heating in the sealed tubes or to the high temperature of distillation. In order to determine, therefore, whether these operations are of fundamental importance in deciding the composition of the substance which we have isolated, we made a mixture of 30 grams of ethyl tartrate and 90 grams of chloral, allowing one-half to remain at the ordinary temperature, whilst the other half was heated in a sealed tube for ten hours at 130°. After five days the former gave $\alpha_D + 30{\cdot}5°$, whilst the latter had $\alpha_D + 32{\cdot}62°$. It seems probable, therefore, that the condensation product is formed at the ordinary temperature to very much the same extent as it is formed in the sealed tube.

It seemed also desirable to ascertain whether, on heating with chloral, the carbon chain contained in ethyl tartrate was ruptured or whether any racemisation took place. A fresh specimen of the condensation product was prepared by heating 90 grams of ethyl tartrate with 200 grams of chloral in sealed tubes at about 130—140° for a day. On distillation and crystallisation from light petroleum some 15 grams of the condensation product were obtained. It was recrystallised twice from light petroleum, and then melted at 68°. Three grams of this sample were heated under a reflux condenser with slight excess of methyl-alcoholic potassium hydroxide for about two hours. After evaporation of the alcohol the solid residue, which weighed approximately 2 grams, was placed in a flask along with 15 c.c. of *iso*butyl alcohol, and hydrogen chloride passed, during some four hours, into the mixture, which was, at the same time, heated on the water-bath. Ether was then added to the contents of the flask, the insoluble potassium chloride collected, and the ether removed. On distillation under diminished pressure, after previous crystallisation from light petroleum, 0·6 gram of pure *iso*butyl tartrate was obtained, melting at 73°. Of this substance 0·302 gram, made up to 15 c.c. with nitrobenzene, gave $\alpha_D^{15\cdot6}$(200 mm.) +2·305°, whilst a pure specimen of the ester from tartaric acid had α_D^{16}(200 mm.) +2·32°. It appears, therefore, that the carbon chain in the ethyl tartrate remains intact.

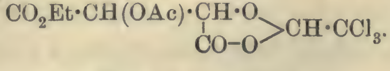
Part of this specimen was redistilled under 6 mm. pressure, and boiled at 170°. The rotation of the sample thus obtained was then examined at a number of temperatures with the following results:

Condensation Product of Ethyl Tartrate and Chloral.

t	72·0°	82·1°	97·5°	125·0°	164·5°
d	1·4322	1·4201	1·4022	1·3710	1·3252
$\alpha_D^{t°}$	+57·97°	+57·11°	+56·13°	+53·65°	+48·75°
$[\alpha]_D^{t°}$	40·48	40·22	40·04	39·19	36·85
$[M]_D^{t°}$	124·5	123·6	123·1	120·3	113·1

The rotation thus diminishes as the temperature rises and at a gradually increasing rate.

Acetyl Derivative of the Condensation Product of Ethyl Tartrate and Chloral,



$$\begin{array}{l}CO_2Et\cdot CH(OAc)\cdot CH\cdot O \\ \qquad\qquad\qquad\quad\;\; CO-O\end{array}\!\!>CH\cdot CCl_3.$$

In order to verify the constitution of the condensation product of ethyl tartrate and chloral, 3 grams of the substance were heated for about one hour with excess of acetyl chloride under reflux. The excess of chloride was then distilled off, and the residue poured into water. After some time it solidified, and was found to crystallise well from light petroleum. The new compound melted at 73—74°. It distilled without decomposition, boiling at 175°/6 mm.

Found: Cl = 30·42.

$C_{10}H_{11}O_7Cl_3$ requires Cl = 30·47 per cent.

There is thus no doubt that the condensation product contains a hydroxyl group which can react with acetyl chloride.

The rotation of this acetyl derivative was then determined at a number of different temperatures with the following results:

Acetyl Derivative of Condensation Product.

t	82·2°	102·4°	125·0°	164·5°
d	1·364	1·3405	1·314	1·267
$\alpha_D^{t°}$	+38·89°	+36·38°	+35·40°	+32·62°
$[\alpha]_D^{t°}$	28·16	27·51	26·95	25·75
$[M]_D^{t°}$	98·4	96 1	94·2	90·0

The rotation thus diminishes, practically linearly, as the temperature rises. It will be noticed that both the specific and the molecular rotations of the acetyl derivative are less than that of the condensation product, which affords another example of the regularity already referred to on p. 790.

A small quantity of this acetyl derivative was then dissolved in chloral to make a p = 4·27 solution. This gave in a 50 mm. tube at 26° an observed rotation of +1·01°, in which, after two days, no change could be detected. When the hydroxyl groups are completely saturated, therefore, the compound remains unattacked by chloral.

Some of the condensation product itself was then dissolved in chloral, and the solution, of p = 17·79, examined polarimetrically.

Condensation Product of Ethyl Tartrate and Chloral in Chloral.

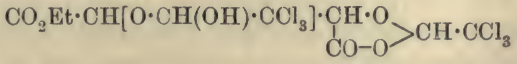
T (mins.).	α_D^{26} (100 mm.).	T (mins.).	α_D^{26} (100 mm.).
5	+10·20°	1953	+13·20°
33	10·266	2743	14·00
123	10·544	3063	14·204
226	10·72	(days)	
296	10·884	3	15·18
523	11 388	4	16·02
1313	12·444	9	17·824
1578	12·82	13	18·28
1748	13·10	∞	18·28

In the compound with a free hydroxyl group, the rotation changes to a very considerable extent with lapse of time, and as will be noticed, the alteration is only slow with no reversal of sign, so that it corresponds very closely with the second rise of rotation of the original experiments with ethyl tartrate and chloral. The mixture used in the above experiment was poured into an evaporating basin, and allowed to remain in an exhausted desiccator over sulphuric acid until all the chloral had evaporated. In the course of some two months the residue had become pasty owing to the separation of solid. It was extracted with light petroleum, from which, on cooling, there separated crystals melting at 66—68°. On mixing a small quantity of this with the condensation product, the melting point remained unaltered, and on dissolving these crystals in chloral again and examining the solution in the polarimeter, the rotation was found to increase as before.

$p=2{\cdot}41$:

T (mins.).	α_D^{26}.
15	+1·40°
330	1·666
525	2·20
1360	2·52
4 days	2·60

It seems thus to be clear that the condensation product is attacked by chloral in the same manner as ethyl tartrate, but that the reaction does not go so far. Chloral is added on at the hydroxyl group to form

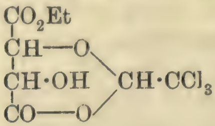


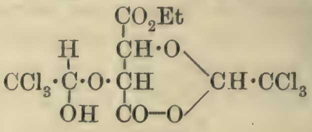
$$CO_2Et{\cdot}CH[O{\cdot}CH(OH){\cdot}CCl_3]{\cdot}\begin{matrix}CH{\cdot}O\\ |\\ CO{-}O\end{matrix}\!\!>CH{\cdot}CCl_3$$

but no second elimination of a molecule of alcohol takes place. The chloral appears to be very feebly combined, and to be split off again on distillation and on crystallisation, which accounts for the formation of only the mono-chloralated product, even after several energetic treatments with chloral in sealed tubes.

From our experiments, therefore, there seems to be little doubt that the action of chloral on ethyl tartrate consists of three processes. First, the addition of a molecule of chloral at one of the hydroxyl groups; secondly, the elimination of a molecule of alcohol between the hydroxyl group now attached to the chloral part of the molecule and the carbethoxy-group, causing a gradual fall of rotation; and thirdly, addition of a second chloral molecule at the remaining hydroxyl group, causing a new rise of rotation. At this point the reaction stops; if the product is distilled, the second molecule of chloral is split off again. These three reactions doubtless go on together with different velocities. The fact that no second condensation takes place is probably a result of steric hindrance.

It may just be mentioned that in addition to compounds represented by the formulæ we have adopted, others are possible, namely, I for the condensation product, and II for the final equilibrium product with chloral. We are not in a position, however, to discriminate between these. Further, since the carbon atom, originally belonging to the aldehyde group of the chloral molecule, becomes asymmetric in the reactions we are dealing with, there are still other openings for isomerism. The condensation product we have isolated may be a homogeneous individual containing three asymmetric atoms or it may be partly enantiomorphic. It is possible that one configuration of the radicles around the new asymmetric atom might be produced in preference to the other, and this might be the cause of the high rotations of the compounds produced. In the hope of perhaps being able to effect a new asymmetric synthesis, we made up a solution of 3 grams of the condensation compound in 40 grams of methyl alcohol, and examined the rotation of the solution from time to time.* It had α_D^{20}(400 mm.) $+9°$ initially, and in the course of six months fell to $+3·6°$. The methyl alcohol was then distilled off at as low a temperature as possible and under diminished pressure. Any active chloral alcoholate that had been formed would be in this distillate, but since the solution was quite inactive we must conclude, either that chloral does not combine with ethyl tartrate in one configuration in preference to the other, or, if an asymmetric synthesis is accomplished, the chloral methyl alcoholate formed racemises again, and this, of course, would be very likely.


(I.)


(II.)

Ethyl Malate in Chloral.

Having thus elucidated to our satisfaction the behaviour of ethyl tartrate and chloral, we again turned our attention to that of ethyl malate and chloral. As will be remembered, the rotation of a $p=14·81$ solution diminished rapidly to reach a minimum of $-16·35°$ in two hundred and twenty minutes, rising again in the course of about a week to $-13·2°$. A fresh solution was made of 50 grams of ethyl malate and 120 grams of chloral, $p=29·4$, part of this mixture being heated in a sealed tube for twenty-four hours at 130°, whilst another part was kept in a sealed tube at the ordinary temperature. After a week the rotation of both was determined:

Liquid after heating to 130°: $\alpha_D^{26} -4·72°$.
Liquid at ordinary temperature: $\alpha_D^{26} -26·50°$.

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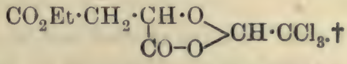
* Compare Gadamer, *ante*, p. 788.

The rotation of the portion that had remained at the ordinary temperature thus corresponds very closely with that which had been observed formerly in the case of the more dilute solution, but apparently the effect of heating in a sealed tube is much greater with the malate than with the tartrate. The contents of the tube which had been heated were then distilled under diminished pressure.* The fraction collected from 140—160°/13 mm. gave $\alpha_D^{26} + 1{\cdot}76^\circ$, and that from 160—180°/13 mm. gave $\alpha_D^{26} + 15{\cdot}50^\circ$. The product isolated from the slightly lævorotatory solution is thus fairly strongly dextrorotatory. The second fraction on keeping deposited a solid, which crystallised readily from light petroleum in glistening plates melting at 55°. This compound distilled easily under diminished pressure, boiling at 150°/6 mm.

Found: $Cl = 35{\cdot}86$, $35{\cdot}92$.

$C_8H_9O_5Cl_3$ requires $Cl = 36{\cdot}53$ per cent.

There could be little doubt, therefore, that the substance was the condensation product of formula



$$CO_2Et\cdot CH_2\cdot\begin{matrix}CH\cdot O\\ |\\ CO-O\end{matrix}\!>CH\cdot CCl_3.\dagger$$

analogous to that of the substance obtained from ethyl tartrate. After a further crystallisation from light petroleum we found $Cl = 36{\cdot}48$ per cent., almost in exact agreement with theory.

A portion of the specimen that had been distilled was hydrolysed by boiling with alcoholic potassium hydroxide, and the potassium salt converted into *iso*butyl malate just as described for the corresponding tartrate. The ester obtained boiled at 160°/13 mm., and had $\alpha_D^{12\cdot1} - 10{\cdot}56^\circ$, whilst a specimen prepared in an exactly similar manner from malic acid had $\alpha_D^{10} - 10{\cdot}85^\circ$. In spite, therefore, of the change of sign of rotation due to the condensation, there is no racemisation.

For further verification, the *iso*butyl malate obtained from the chloralate was heated at 160° for eight hours with excess of aniline. The anilide formed melted at 195—196°, and, when dissolved in glacial acetic acid ($c = 1{\cdot}49$), gave $[\alpha]_D^{26} - 62{\cdot}34^\circ$. Walden (*Zeitsch. physikal. Chem.*, 1895, **17**, 250) quotes for this compound,

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* The formation of chloral alcoholate was again observed, as in the case of ethyl tartrate.

† While this paper was in the press we found that a similar compound had been prepared by Wallach and Heymer (*Ber.*, 1876, **9**, 545) from ethyl lactate and chloral, and from trichlorolactic acid and chloral (see also Wallach and Reincke, *Ber.*, 1876, **9**, 1215; 1877, **10**, 2128; Klimenko, *J. pr. Chem.*, 1877, [ii], **13**, 98). Wallach and Hansen (*Ber.*, 1876, **9**, 1214) describe a monochloralate of malic acid and a dichloralate of tartaric acid. From our experiments the existence of the latter, at least, would seem to be improbable.

m. p. 196°, and for the solution in glacial acetic acid ($c = 1{\cdot}50$), $[\alpha]_D^{20}$ $-60{\cdot}66°$.

A solution of this ethyl malate condensation product was then made up with chloral, of $p = 4{\cdot}93$. It showed a rotation α_D^{26} $+2{\cdot}50°$, which did not alter on keeping.

The rotation of the ethyl malate condensation product was determined at a number of different temperatures, the distilled sample being used. The results were as follows:

Rotation Condensation Product of Ethyl Malate–Chloral.

t	41·6°	60·1°	90·1°	123·0°	161·5°
d	1·4246	1·4025	1·3690	1·3295	1·2800
$\alpha_D^{t°}$	+39·53°	+36·70°	+32·33°	+28·16°	+23·68°
$[\alpha]_D^{t°}$	27·81	26·16	23·61	21·15	18·50
$[M]_D^{t°}$	81·07	76·3	68·82	61·66	53·93

The rotation of the ester thus diminishes rapidly on heating, but at a slightly decreasing rate as the temperature rises.

From the experiments we have carried out it seems quite certain that the action of chloral on ethyl malate is exactly analogous to its action on ethyl tartrate. We find here, however, only two processes: first, an addition of chloral at the hydroxyl group, and secondly, the elimination of a molecule of alcohol. The first reaction is accompanied by a large diminution of rotation, whilst the second produces a much greater increase, the rotation becoming highly positive. When a mixture of ethyl malate is kept at the ordinary temperature, the second process does not go very far, the high negative rotation of the primary product much exceeding the positive rotation of such condensation product as is formed. On heating in a sealed tube, the condensation product is formed to a much greater extent.

One other matter may be briefly referred to. The first process, both in the case of the tartrate and of the malate, and the third step in the case of the tartrate, furnish excellent examples of true addition reactions, genuine instances of chemical combination of solute with solvent. In the tartrate both additions are accompanied by increase of rotation; in the malate the addition is accompanied by diminution of rotation; in all cases, however, these are *slow* changes; they can be followed with ease in the polarimeter, and could be measured with accuracy. It is of interest to compare them with the solvent influence of chloral. Turning to table I it will be seen clearly from the figures for solution II, for example, that the solvent influence of chloral on ethyl tartrate is negative, that is, tends to depress the rotation below that of the homogeneous ester. It is thus exactly the opposite of the effect which is produced by actual chemical combination, and, moreover, it is exerted, so far as it is possible to judge, instantly. The two effects thus seem to be very sharply contrasted, and to be of a different order entirely.

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LXXXIV.—*Purpurogallin. Part II.*

By ARTHUR GEORGE PERKIN.

PREVIOUS work (Perkin and Steven, Trans., 1903, **83**, 192) has indicated that purpurogallin, the interesting oxidation product of pyrogallol, and which is apparently a naphthalene derivative (Nietzki and Steinmann, *Ber.*, 1872, **5**, 848), most probably possesses the simple formula $C_{11}H_8O_5$, and although at present it is not easy to speculate as to the course of the remarkable reaction thus involved, it is likely that the compound $C_6H_4O_3$, obtained from pyrogallol by means of *iso*amyl nitrite (Trans., 1906, **89**, 802), may represent its earliest stage.

When digested with concentrated potassium hydroxide solution, purpurogallin yielded in small amount two apparently isomeric compounds, namely, purpurogallone and *iso*purpurogallone, for which the formula $C_{11}H_6O_5$ was suggested, and a preliminary account of the reinvestigation of these compounds has been given (Proc., 1905, **21**, 211). Owing to pressure of other work, and the difficulty of accumulating a sufficient stock of the raw material, the matter has remained almost at a standstill, and it thus appeared wise as soon as possible to communicate to the Society some new facts which have recently been obtained.

EXPERIMENTAL.

The purpurogallin employed in this investigation was prepared by the electrolytic oxidation of pyrogallol (A. G. and F. M. Perkin, Trans., 1904, **85**, 244), the most convenient method for obtaining it in quantity. It was purified by crystallisation from much acetic acid, although for some purposes the pure acetyl derivative was prepared, and subsequently submitted to hydrolysis by means of hydrochloric acid in the presence of acetic acid.

Purpurogallone and iso*Purpurogallone.*

The process originally employed for the preparation of these compounds consisted in boiling purpurogallin with 50 per cent. potassium hydroxide solution in an open flask until the temperature reached 170°, the yield thus averaging 25 per cent. of the crude mixture. By this method it was likely that some loss of product by air oxidation occurred during the earlier period of the digestion, and as the result of experiment, the following process was eventually adopted.

To a solution of 60 grams of potassium hydroxide in 20 c.c. of water at a temperature of 170° in an open flask, 10 grams of purpurogallin were cautiously added, and the mixture was heated gradually to 190°. When a sample of the product dissolved in water gave, on shaking, the deep red colour characteristic of the purpurogallones, and no green tinge due to purpurogallin could be detected, the mass was allowed to cool to 120°, treated with a little water, and poured into much hot dilute sulphuric acid. A small amount of a black precipitate separated, and this was at once removed, and the clear, yellowish-brown liquid allowed to remain for about three days. The dull, yellow, crystalline deposit (5·5—6 grams) was collected, and in concentrated alcoholic solution poured into much ether, the ethereal solution being well washed and evaporated. (Yield, 5 grams.) By shaking the acid filtrate from the crude purpurogallones with ether, about 1 gram of substance could be also isolated, the total yield thus averaging 60 per cent. As previously stated, purpurogallone is best separated from the more soluble *iso*purpurogallone by fractional crystallisation from alcohol, and the progress of this is easily traced, by acetylating a minute portion of each fraction, for whereas the *iso*purpurogallone compound melts at 284—286°, that from purpurogallone melts at 174—176°. By the former method of working a large amount of *iso*purpurogallone was usually produced, but by this newer process only 10 to 15 per cent. is formed, and this is preferably separated from the final mother liquor by dilution with hot water.

As thus prepared, purpurogallone frequently contains traces of purpurogallin, which still contaminate it, even after repeated recrystallisation. To remove the latter the mixture is dissolved in dilute alkali in absence of air, and carbon dioxide passed to saturation, by which means the purpurogallin alone is precipitated, and is best removed by shaking with ether. From the sodium bicarbonate solution, hydrochloric acid deposits purpurogallone.

The earlier analyses of purpurogallone gave figures intermediate between those required for the formulæ $C_{11}H_8O_5$ and $C_{11}H_6O_5$, the latter being at the time preferred, and a molecular-weight determination also approximated with these formulæ. Analyses since carried out of the substance itself, and more especially of its derivatives, show, however, that in reality $C_{11}H_8O_5$ is preferable.

Found: C = 60·05, 59·99; H = 3·86, 3·73.

$C_{11}H_8O_5$ requires C = 60·00; H = 3·63 per cent.

When purified by the above-described method, purpurogallone melts at about 262—264°, but as obtained by the hydrolysis of the pure acetyl compound, the melting point is 271—273°.

On acetylation, acetylanhydropurpurogallone is produced, melting at 174—176° (*loc. cit.*), and this has not again been analysed, as the former figures are in close agreement with the formula $C_{11}H_4O_4(C_2H_3O)_2$.

Methylation of Purpurogallone.—Purpurogallone dissolved in methyl alcohol was treated with equivalent quantities of methyl sulphate and potassium hydroxide, and the operation repeated until no change of colour could be noted on the addition of the latter. The product diluted with water was extracted with ether, the ethereal liquid washed with dilute alkali, and evaporated. A hot alcoholic solution of the residue at first deposited a small amount of colourless needles melting at 211—212°, but the main product obtained on concentration consisted of prisms, which when pure melted at 81—83°.

Found: C = 64·96; H = 6·05; Me = 21·48.

$C_{11}H_4O_5Me_4$ requires C = 65·21; H = 5·80; Me = 21·73 per cent.

Examination showed that this more readily soluble compound is *methyl purpurogallone trimethyl ether*, $C_{15}H_{16}O_5$, whereas the substance of higher melting point consists of the iso*purpurogallone methyl ether* described below. The formation of the latter during the methylation process caused at first considerable doubt as to the individuality of the purpurogallone itself, but as numerous samples purified by diverse methods always gave a similar result when methylated, another cause eventually suggested itself, and this is discussed later.

The fact that purpurogallone dissolves in sodium bicarbonate solution, and also readily in aqueous potassium acetate, indicated the presence in this substance of a carboxyl group, and experiments were now carried out with the object of preparing an ester. The substance (3 grams) was suspended in alcohol (75 c.c.), and hydrogen chloride passed to saturation. After remaining overnight, the clear liquid was poured into ether, the mixture repeatedly washed with sodium bicarbonate solution, and evaporated. By crystallisation from dilute alcohol the substance was obtained in yellow leaflets, and was further purified by recrystallisation from benzene.

Found: Et=11·74.

$C_{11}H_7O_4{\cdot}OEt$ requires Et=11·69 per cent.

Purpurogallone ethyl ester, $C_{13}H_{12}O_5$, melts at 151—153°, and is obtained only in small amount by this method. Although a trace of a second compound melting about 124—125° was also produced, and is most probably the *diethyl* compound, approximately half the original quantity of purpurogallone could be recovered unchanged. The ester is soluble in dilute alkalis with a yellow colour, and from this solution in absence of air the original compound can be precipitated by carbon dioxide. With acetic anhydride it gives an acetyl derivative, which when crystallised from alcohol forms colourless, prismatic needles melting at 126—127°.

Purpurogallonedianilide is produced when purpurogallone (1 gram) is digested with boiling aniline (5 c.c.) for half an hour. The solution is poured into dilute hydrochloric acid, and the resulting grey-coloured precipitate collected and crystallised from benzene or alcohol.

Found: C=74·46; H=4·67; N=7·69.

$C_{23}H_{18}O_3N_2$ requires C=74·59; H=4·86; N=7·57 per cent.

It consists of colourless leaflets melting at 202—203°, sparingly soluble in alcohol, and with which on long boiling it suffers decomposition, a deep green liquid being produced.

When distilled with zinc dust, purpurogallone gives a small amount of an oily distillate, which solidifies on keeping. The product, drained on tile, crystallised from light petroleum, and finally sublimed, was obtained in leaflets melting at 77—79°, having the properties of naphthalene. This result was interesting as an indication that in the production of purpurogallone from purpurogallin, which also gives naphthalene (Nietzki and Steinmann, *Ber.*, 1887, **20**, 1277), no radical transformation in structure occurs.

If purpurogallone, made into a thin cream with boiling acetic acid, is treated drop by drop with sulphuric acid, a red-coloured solution is at first produced, which, however, quickly becomes semi-solid, owing to the separation of colourless needles. This compound, which is evidently *anhydropurpurogallone*, the acetyl derivative of which is described above, owing to its somewhat ready solubility in cold acetic acid was not isolated in the pure condition. It is analogous to the anhydro*iso*purpurogallone described later, and when acetylated gives, as anticipated, the acetyl derivative melting at 174—176°.

iso*Purpurogallone*, produced in but small amount from purpurogallin by the method described, was purified by recrystallisation from dilute alcohol. Analysis gave C = 60·08; H = 3·54 per cent., figures again approximating with those yielded by purpurogallone, whereas its anhydroacetyl compound was found to melt at 284—286°, a temperature which is slightly higher than that previously indicated (280—282°). *iso*Purpurogallone is not precipitated from alkaline solutions with carbon dioxide, and is, moreover, soluble in solutions of the alkali acetates.

Addition of sulphuric acid to its solution in boiling acetic acid caused the separation of a crystalline precipitate, which was collected and washed with acetic acid.

Found: C = 65·36; H = 2·80.

$(C_{11}H_5O_4)_2$ requires C = 65·67; H = 2·49 per cent.

*Anhydro*iso*purpurogallone* consists of minute, yellow prisms, very sparingly soluble in acetic acid, and melting above 310°. In the earlier investigation boiling acetic acid was employed for the purification of both purpurogallone and *iso*purpurogallone. The somewhat higher figures given by these former preparations indicate as probable that in these circumstances a partial conversion into the anhydro-compound takes place, and during the present work the use of acetic acid for this purpose has been avoided.

The *tetramethyl* compound of iso*purpurogallone*, $C_{30}H_{30}O_{10}$, is readily obtained by the use of a large excess of methyl sulphate and alkali, proceeding in the ordinary manner. The product, insoluble in alkali, was crystallised from alcohol.

Found: C = 65·53, 65·57; H = 5·62, 5·51; Me = 21·41.

$(C_{11}H_8O_5Me_4)_2$ requires C = 65·46; H = 5·46; Me = 21·81 per cent.

It consisted of small, colourless needles melting at 210—212°, and was identical with the compound produced in small amount, together with methyl purpurogallone trimethyl ether during the methylation of purpurogallone. In this case it is the sole product of the reaction. It is unchanged by boiling with dilute alkali.

iso*Purpurogallone diethyl ester*, $C_{30}H_{32}O_{10}$.—An alcoholic solution of *iso*purpurogallone was saturated with hydrogen chloride, and allowed to remain for several hours. The product was poured into ether, the solution washed, evaporated, and the residue extracted with benzene. The concentrated benzene extract on cooling deposited crystals, which were recrystallised from the same solvent.

Found: Et = 11·74.

$(C_{11}H_6O_5Et_2)_2$ requires Et = 11·74 per cent.

It consisted of pale yellow, almost colourless leaflets melting at 217—218°. The product insoluble in benzene was found to consist of unattacked *iso*purpurogallone.

Conversion of Purpurogallone into iso*Purpurogallone.*

When purpurogallone is heated on the water-bath with sulphuric acid a deep red liquid is produced, which gradually becomes semi-solid. Addition of water causes the separation of a deep red precipitate, and this was collected, dissolved in excess of dilute alkali, the solution neutralised with acid, and filtered. The filtrate, when shaken with ether, yielded a small quantity of a yellow, crystalline substance, and from its general reactions and the melting point of the acetyl derivative (282—284°) this was found to consist of *iso*purpurogallone. The yield was approximately 12 per cent.

The result of this experiment, in conjunction with the formation of the tetramethyl compound of *iso*purpurogallone when purpurogallone is methylated, suggested that the material employed contained in reality both substances, the latter in this case being more readily attacked by the acid. In a second trial, however, the evolution of a small quantity of sulphurous acid was noted, suggesting that this change might arise from oxidation.

Some purpurogallone was therefore treated with a little persulphate in ice-cold sulphuric acid solution. The dark-coloured liquid, when poured into water and extracted with ether, gave a brownish-yellow product, which yielded with acetic anhydride, a yellow, crystalline powder melting at about 280°, and this by extraction with benzene and concentration of the extract, gave colourless crystals of acetylanhydro*iso*purpurogallone. By this method the yield was hardly greater than with sulphuric acid at 100°, and it was evident in both cases that the reaction proceeded mainly in other directions.

Ultimately, oxidation with potassium ferricyanide gave a satisfactory result. Purpurogallone (1 gram) dissolved in potassium acetate solution (3 grams in 40 c.c. of water) was treated with a solution of 1 gram of the ferricyanide in 15 c.c. of water, the mixture allowed to remain overnight, acidified, and the yellow precipitate collected. This, when dry, weighed 0·75 gram, and consisted of nearly pure *iso*purpurogallone. The acetyl compound melted at 284—286°, and when admixed with acetylanhydro*iso*purpurogallone prepared by means of purpurogallin and alkali, showed no alteration in melting point. (Found, C = 62·95; H = 3·31 per cent.)

As *iso*purpurogallone is obtained by the oxidation of purpurogallone, and the analytical figures given by both are very similar, it was evident that the latter must possess either the formula $C_{11}H_6O_5$ or the formula $C_{22}H_{14}O_{10}$. As the acetyl derivative is too sparingly soluble for examination by the cryoscopic method, the tetramethyl compound of *iso*purpurogallone was accordingly employed:

0·6450 in 14·36 of naphthalene gave Δ^t 0·585. M.W. = 537.
$C_{22}H_6O_5Me_8$ requires M.W. = 550.

*iso*Purpurogallone is therefore to be represented by the formula $C_{22}H_{14}O_{10}$, and is derived from two molecules of purpurogallone by the abstraction of two atoms of hydrogen. In other words, as purpurogallone is a naphthalene compound, *iso*purpurogallone is to be regarded as a derivative of dinaphthyl. The production of the tetramethyl compound of the latter during the methylation of purpurogallone is evidently therefore due to air oxidation, and this must take place very readily under alkaline conditions. It has indeed been found that some *iso*-compound is formed when a solution of purpurogallone in aqueous alkali is exposed to air, but the action in this case is apt to proceed too far, and the best conditions have not as yet been ascertained.

Action of Alcoholic Potassium Hydroxide on Purpurogallin Trimethyl Ether.—The result of a preliminary study of this reaction is given in the earlier paper, a colourless acid being thus produced in small quantity. As the production of the trimethyl ether from purpurogallin by means of methyl iodide (*loc. cit.*) is difficult, and the yield unsatisfactory, experiments with methyl sulphate were carried out, and the following process eventually adopted. Ten grams of purpurogallin added to 225 c.c. of methyl alcohol diluted with 25 c.c. of water were treated with 50 c.c. of methyl sulphate and 33 grams of potassium hydroxide in four distinct portions, the mixture being heated to boiling after each addition. Finally, the product was diluted with 50 c.c. of hot water, allowed to remain overnight, and the crystals of purpurogallin trimethyl ether which had then separated were collected and washed with dilute alkali. The product was sufficiently pure for most purposes, and after one crystallisation from alcohol was chemically pure. Yield, 5·85 grams.

Found: C = 64·05; H = 5·43 per cent.

The dilute alcoholic filtrate from the purpurogallin trimethyl compound on partial evaporation gave, on extraction with ether, a product consisting chiefly of purpurogallin tetramethyl ether, and from which 2·5 grams of the latter substance were obtained.

Two grams of purpurogallin trimethyl ether, dissolved in 15 c.c. of 10 per cent. alcoholic potassium hydroxide, were heated in a sealed tube for two hours at 160—170°. The dark-coloured solution was evaporated, dissolved in water, and the liquid saturated with carbon dioxide, which caused the precipitation of a dull yellow, resinous precipitate, and this was removed by shaking with ether. The aqueous solution, when neutralised with acid, gradually deposited 0·45 gram of a crystalline powder, which was recrystallised from dilute alcohol.

Found: C=62·87, 63·01; H=5·07, 4·99; Me=12·09.
$C_{13}H_{12}O_5$ requires C=62·90; H=4·84; Me=12·10 per cent.

It was obtained in colourless, prismatic needles, and melted, as previously indicated, at 197—199°.

When strongly heated it gave a sublimate melting at 164—166°, but this compound can be more economically prepared by digesting the acid with a little boiling acetic anhydride. From this solution it was deposited by addition of alcohol, and was purified by recrystallisation from the same solvent, being obtained in pale yellow needles.

Found: C=67·51; H=4·52.
$C_{13}H_{10}O_4$ requires C=67·82; H=4·35 per cent.

A trace of the acid $C_{13}H_{12}O_5$ dissolved in methyl alcohol was methylated by means of methyl sulphate and alkali, the product isolated by means of ether, and crystallised from alcohol. It consisted of colourless prisms melting at 80—82°, and was evidently identical with methyl purpurogallone trimethyl ether.

The substance $C_{13}H_{12}O_5$ must therefore be *purpurogallone dimethyl ether*, and the compound $C_{13}H_{10}O_5$ derived from it, *anhydropurpurogallone dimethyl ether.*

With boiling alcoholic potassium hydroxide purpurogallin trimethyl ether gives traces only of this dimethyl ether, for the main product of the reaction consists of the yellow, resinous substance referred to above.

Purpurogallin tetramethyl ether, obtained as a by-product during the preparation of the *trimethyl* compound, is readily prepared by the action of methyl sulphate and alkali on the latter in the usual manner. When pure it separates from alcohol or carbon disulphide in colourless prisms melting at 93—94°, but it frequently retains a trace of the trimethyl ether, which gives it a faint yellow appearance. The latter may, however, be removed by adding to the product dissolved in acetic acid a few drops of chromic acid solution.

Found: C=65·18; H=5·90; Me=21·57.
$C_{11}H_4O(OMe)_4$ requires C=65·21; H=5·79; Me=21·74 per cent.

When heated with alcoholic potassium hydroxide at 160—170°, purpurogallin tetramethyl ether yields a trace of a crystalline acid, and this, which is probably a derivative of purpurogallone, will be further studied when opportunity occurs.

Preliminary experiments indicate that by the action of boiling aniline purpurogallin yields an anilino-compound. The product of the reaction yielded on extraction with benzene a small quantity of a substance crystallising in fine, orange-red needles melting at about 189—191°; but as analysis gave but 3·75 per cent. of nitrogen, whereas the compound $C_{11}H_6O_4{\cdot}NH{\cdot}C_6H_5$ requires 4·74 per cent., apparently further purification was necessary.

Action of Hydriodic Acid on Purpurogallone.—Purpurogallone (2 grams) in 50 c.c. of hydriodic acid (D 1·7) was heated to boiling for one and a-half hours. The substance gradually dissolved, and after a time some quantity of a resinous substance separated. On addition of water containing a little sodium bisulphite, the latter was isolated as a greyish-black, amorphous mass (0·8 gram), which fused below 100°. Ether removed from the clear acid liquid a crystalline product, which when extracted with boiling carbon disulphide only partly dissolved, leaving a small amount of a pale brown residue (A). After some time a trace of (A) was deposited by the extract, which was collected apart, and the filtrate on partial evaporation gave a crystalline product melting at about 133—135°, the aqueous solution of which gave with ferric chloride a deep blue coloration. From the mother liquid two further fractions melting respectively at 125—126° and 115—118° were isolated, so that it was evident that one or more substances were present. By repeated crystallisation from carbon disulphide two fractions among others were obtained, (*a*) melting at 145—148° and (*b*) at 131—132°, and these were submitted to analysis:

(*a*) Found: $C=76{\cdot}33$; $H=5{\cdot}44$. (*b*) Found: $C=80{\cdot}87$; $H=5{\cdot}55$.
$C_{10}H_8O_2$ requires $C=75{\cdot}00$; $H=5{\cdot}00$; and $C_{10}H_8O$ requires
$C=83{\cdot}33$; $H=5{\cdot}55$ per cent.

These results indicated as probable that these fractions consisted of mixtures of mono- and di-hydroxynaphthalenes, and by a laborious series of recrystallisations a substance melting at 122—126°, resembling β-naphthol, and a compound melting at 156—158°, similar in properties to 2:3-dihydroxynaphthalene, were isolated. Subsequently by the employment of alcoholic lead acetate it was found that a complete separation could be more economically effected. When the lead precipitate, thoroughly washed with alcohol, was decomposed with dilute sulphuric acid, the mixture gave, on extraction with ether, a substance which, after recrystallisation from benzene, melted at 161—162°, and gave a deep blue coloration with ferric chloride. It had the properties assigned to 2:3-dihydroxynaphthalene by Friedländer and Zakrzewski (*Ber.*, 1894, **27**, 762), to which the melting point 160—161° is given. The *acetyl* compound, which does not appear to have been previously described, crystallises from alcohol in short, prismatic needles melting at 104—105°.

The filtrate from the lead compound on dilution with a little water gave a pearly, crystalline precipitate, which after washing with water, melted at 120—122°, gave no coloration with dilute ferric chloride, but yielded with benzenediazonium chloride a red benzeneazo-derivative. It had the properties of β-naphthol, and its identity with this substance was confirmed by means of a mixed melting-point determination and a preparation of the acetyl compound which was found to melt at 69—70°.

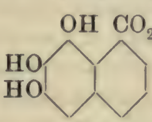
The substance (A), characterised by its insolubility in boiling carbon disulphide and benzene, was crystallised from dilute alcohol, and then commenced to sinter at 270°, and melted at 280—285° with apparent decomposition. It readily dissolves in alkaline solutions, and from these when hot it is deposited in colourless needles. With ferric chloride it gave a deep blue coloration. Carbon dioxide does not precipitate it from alkaline solutions, and it thus appears to contain a carboxyl group. It does not correspond in property with any of the naphtholcarboxylic acids, and may consist of a 2:3-dihydroxynaphthalenecarboxylic acid. The acetyl compound melted at about 178—180°, but sufficient of this or of the substance itself have not yet been available for analysis.

Clermont and Chautard (*Jahresb.*, 1882, 682) found that when purpurogallin itself was heated with hydriodic acid a mixture of hydrocarbons, $(C_{10}H_{14})_x$, was produced. Preliminary experiments employing hydriodic acid (D 1·7) have shown that in addition to a resinous product, phenolic substances are formed, and these will be further investigated.

Summary.

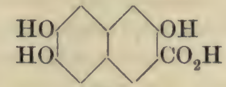
As the result of this and the preceding communications, it is shown that purpurogallone, $C_{11}H_8O_5$, contains three hydroxyl groups, and readily yields an inner anhydride under the influence of dehydrating agents. With zinc dust it gives naphthalene; with hydriodic acid β-naphthol, 2:3-dihydroxynaphthalene, and a substance which is possibly a 2:3-dihydroxynaphthalenecarboxylic acid, so that there can be no doubt that it is a naphthalene derivative. Purpurogallone dissolves in solutions of the alkali bicarbonates and acetates, yields with alcoholic hydrogen chloride a monoethyl derivative insoluble in the former, and these facts, together with others given in the paper, indicate the presence of a carboxyl group in this compound. Peculiar in this respect, how-

ever, is the stability of methyl purpurogallone trimethyl ether towards boiling dilute alkaline solutions, for in preliminary experiments little or no ester hydrolysis has been thereby found to occur, although it is possible that more detailed work will afford an explanation of this apparent anomaly. The main evidence strongly suggests that purpurogallone is a *trihydroxynaphthalenecarboxylic acid* containing two of its hydroxyl groups in the 2:3-positions, whereas *iso*purpurogallone, so readily prepared from it by oxidation, is the corresponding *hexahydroxydinaphthyldicarboxylic acid.* It is indeed likely that purpurogallone is a derivative of naphthapyrogallol, for according to Zincke and Noak (*Annalen*, 1897, **295**, 17) and Zincke and Ossenbeck (*Annalen*, 1899, **307**, 3) alkaline solutions of the latter develop in the air a dark cherry-red coloration, a reaction which is almost identical with that of purpurogallone itself. Until further evidence is forthcoming, and in view of its production from purpurogallin, the following constitution (I) is provisionally suggested for purpurogallone:

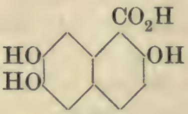


(I.)

Although the yellow colour of this substance indicates a resemblance to 2-naphthol-3-carboxylic acid, in which case formula II would be applicable, an argument against this view is the fact that whereas 2-naphthol-3-carboxylic acid is readily esterified, purpurogallone reacts with extreme difficulty in this manner. As an alternative, the formula III is, however, possible:



(II.)



(III.)

The investigation of purpurogallone and of purpurogallin will be proceeded with as soon as a sufficient supply of raw material is available.

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LXXXV.—*The Use of Phenolphthalein as an Indicator. The Slow Rate of Neutralisation of Carbonic Acid.*

By James William McBain.

As the result of a somewhat elaborate study of the accuracy attainable in the titration of acids with strong alkalis, a number of points have been met with which appear either to have been generally overlooked or not to have been applied to this familiar part of the routine of chemistry. It is therefore hoped that the following collection of quantitative data may be of service, and further may emphasise the very great influence which extraneous carbon dioxide exerts in all such titrations.

In order to obtain comparable results, weighing burettes * were used for stronger solutions, and $N/250$-sulphuric acid and alkali were employed for the final stage of a titration. An essential point was the employment of permanent colour standards for reference. These consisted of 100 c.c. each of a solution of mixtures of copper and cobalt salts (with a large excess of nitric acid to avoid hydrolysis), and contained in Erlenmeyer flasks similar to those employed in the titrations. The weakest solution (No. 1 standard) contained 0·50 gram of cobalt nitrate, $Co(NO_3)_2,6H_2O$, and 0·62 gram of copper sulphate, $CuSO_4,5H_2O$, in a litre; the others (Nos. 2, 3, 4, 5, 6, 7, 8, 10, 15) contained respectively 2, 3, 4, etc., times these amounts. No. 1 to 6 are indistinguishable from the colour of phenolphthalein. For the comparison of colours higher than No. 10 a Donnan colorimeter was employed, using an alkaline "buffer" solution nearly saturated with sodium phosphates and coloured with phenolphthalein, first standardising this "buffer" solution against the above scale. In this way measurements up to a standard corresponding with "No. 200" are readily made. The difference between each standard and the next was originally planned to be equivalent to the colour change caused by the addition of one drop of N/250-acid or alkali.

The Slow Rate of Neutralisation of Dissolved Carbon Dioxide.

Dissolved carbon dioxide, which is present in all titrations, requires about ten minutes for the end-point to come appreciably to rest. This phenomenon appears to have escaped attention, as it has probably been confused with the fading out of the colour of phenolphthalein in the presence of strong alkali. It is elucidated by the following three experiments.

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* Of the form used by E. W. Washburn in his valuable paper on iodimetry, but provided with a guard tube containing stick potassium hydroxide (*J. Amer. Chem. Soc.*, 1908, **30**, 31).

In the first place, within the region of colours Nos. 1 to 20, say, the colour of phenolphthalein after the first hour is constant during many months. This can only be observed if the glass stopper of the containing vessel is well coated with vaseline; otherwise diffusion of carbon dioxide through the ground joint may decolorise the solution within a day.

Secondly, if the solution is boiled out while known to be just acid and then the correct amount of potassium hydroxide free from carbon dioxide is added, the colour is the same after twenty minutes as it was at five seconds; of course, the solution becomes quite colourless just under the surface on account of the gradual diffusion of carbon dioxide from the gaseous phase. This crucial experiment, taken in conjunction with that described above, proves that the fading of the colour observed in titrations is not due to spontaneous changes in the constitution or dissociation of the phenolphthalein. Such constitutional changes take place with measurable rapidity only in much more alkaline solution. Possibly at this concentration of alkali they would take place in the opposite direction—this point was not investigated. Again, it follows that this is not a measurably slow completion of the reaction of neutralisation in general, $H^{\cdot} + OH' = H_2O$; but that it is a property of the carbon dioxide.

Thirdly, the slow fading of the colour cannot be explained away as due to fresh carbon dioxide coming into the solution from the gaseous phase, for the same phenomena are observed if two beakers are taken, one of which fits closely within the second. Here there is no gas space, and yet the same rapid decolorisation within a few minutes takes place, the fading being partial or complete according as to how far away the final end-point lies.

One further experiment was carried out to check the result of the second one above. In three glass-stoppered flasks equal amounts of dilute acid were placed, and to two of these were added twenty drops of stock phenolphthalein solution (neutralised), and these were then titrated to a convenient end-point colour. The same amount of potassium hydroxide was then put into the remaining flask, which contained as yet no phenolphthalein; and after an hour and a-half the same amount of phenolphthalein was added. The result was that the colour in this flask was the same ten seconds afterwards as it was after a further lapse of twenty minutes, showing that the end-point had finished changing before the phenolphthalein had been added.

As to what is the slow stage in the neutralisation of carbon dioxide: it is not the rate of solution which has been studied by several observers, and is in agreement with that predicted; moreover, this has been excluded by the experiment quoted. There remain the rate of hydration of the dissolved carbon dioxide, and the rate of dissociation of the carbonic acid. Carbon dioxide in aqueous solution is usually assumed to be partly anhydrous and partly in the form of a hydrate—say, for example, H_2CO_3. There appears to be no evidence as to which of these two processes—the hydration or the electrolytic dissociation—is the slow reaction, and either would seem possible. The latter alternative would be particularly interesting.

With regard to the actual rate of this neutralisation, there is, of course, no doubt that the reaction proceeds the greater part of the way in a fraction of a minute; but it is sufficiently incomplete to permit of a bright red colour repeatedly vanishing within a few minutes after the first apparent attainment of the end-point. In one experiment with no gas phase (as described above) the colour ten seconds after the last amount of potassium hydroxide had been added was No. 15, at thirty seconds No. 6, at one minute No. 2, at two minutes No. 1, at four minutes colourless. In another in a stoppered flask, well shaken, the colour was No. 15 at six minutes; No. 8 at ten minutes; No. 5 at twelve minutes; No. 3 at seventeen minutes; and No. 3 at thirty-one minutes; a trace of carbonate was known to be present. There is, however, little point in multiplying such instances, since in the absence of carbonate, as already shown, the end-point is instantaneous and permanent; and, again, if much carbonate be present, as in a normal bicarbonate solution, the end-point is likewise practically independent of the time; thus the observed effect is not simple; the significance of a given colour-change varies enormously with the amount of carbonate present, as will be seen.

The Alkalinity of the End-points Reached with Phenolphthalein.

E. Salm (*Zeitsch. physikal. Chem.*, 1907, **57**, 480) has determined the concentration of free alkali in $N/10$-disodium hydrogen phosphate, and in nine hundred and fifty parts of this solution mixed with fifty parts of $N/10$-sodium dihydrogen phosphate. The concentration of hydrogen ion in these solutions was $1{\cdot}3 \times 10^{-9}$ and $1{\cdot}0 \times 10^{-8}N$ respectively at 18—19°. In neutral water at this temperature the hydrogen and hydroxyl concentrations are each equal to $0{\cdot}8 \times 10^{-7}$. The concentration of alkali in the above solutions is therefore $0{\cdot}50 \times 10^{-5}N$ and $0{\cdot}64 \times 10^{-6}N$ respectively. Different solutions differ by a few units, but the first lies at about

No. 150 and the second at about No. 3 on my colour scale*; thus the average colour is fifty times deeper in the former case. It should be noted that colour No. 1 is very distinctly coloured if compared with ordinary water, and that each of these weaker colours is quite distinct from the next, although the first dozen seem almost colourless in comparison with the bright pink, which is more usually chosen as end-point in acidimetry.

The Effect of Carbon Dioxide (Carbonates) on the Sensitiveness of an End-point with Phenolphthalein.

No. 3 standard is $6{\cdot}4 \times 10^{-7} N - OH'$, and No. 150 is $50 \times 10^{-7} N - OH'$. The excess of alkali over exact neutrality ($0{\cdot}8 \times 10^{-7} OH'$) in 100 c.c. each of solutions of this colour, assuming absolutely no weak acids or bases present, is $(6{\cdot}4 \times 10^{-7} - 0{\cdot}8 \times 10^{-7})100/1000$ and $(50 \times 10^{-7} - 0{\cdot}8 \times 10^{-7})100/1000$ gram-equivalents of alkali respectively. These numbers are equivalent to the addition of 0·0006 and 0·005 c.c. of $N/10$-alkali respectively, the difference amounting to 0·0043 c.c. of $N/10$-alkali.

This means that only 0·0043 c.c. of $N/10$-potassium hydroxide should be necessary to change the colour of 100 c.c. of the pale pink solution equal to No. 3 standard to a bright red colour equal to No. 150 standard. This is, however, not experimentally realisable; the presence of any weak acid, owing to hydrolysis, must enormously increase these numbers. This is evident when Salm's phosphate solutions are recalled; the $N/10$-disodium phosphate was equal to No. 150 standard, and if 5 per cent. of this phosphate was replaced by the monosodium compound, it sank to standard No. 3; that is, about 5 c.c. of $N/10$-potassium hydroxide is necessary to effect this colour-change in the presence of this concentration of phosphate—a value more than 1000 times greater than the 0·0043 c.c. predicted in the absence of weak acids.

Carbonate must necessarily have a similar effect, for it cannot be entirely excluded from any titration (100 c.c. of outdoor air contains carbon dioxide equal in amount to at least 0·03 c.c. of $N/10$-potassium hydroxide). The following were the experimental results, using "carbon dioxide free" solutions prepared with some care,* and adding known amounts of carbonate for the last three determinations. The data refer to colours below No. 10 of the colour standard and to 20 drops of phenolphthalein per 100 c.c. The second line of the table refers to ordinary distilled water; Treadwell ("Quantitative Analyse," 1904) estimates the carbon dioxide in distilled water as equivalent to from 0·5 to 1·8 c.c. of *N*/10-potassium hydroxide per 100 c.c.

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* Phenolphthalein, like Congo-red or soap, belongs to the category of electrolytic colloids in which dissociation, coagulation, and hydrolytic equilibria co-exist. Thus the data obtained above may be slightly affected by "neutral salt action." The available experimental data are to the effect that the influence of neutral salts on the dissociation of weak substances is negligible, and presumably the chief disturbance is effected through the medium of the colloids present. Phenolphthalein has been shown to be less sensitive than many other indicators in this respect, and here the solutions are dilute and comparable. In any case the essential object was to obtain definite points of reference which must be nearly quantitative.

Concentrations of carbonate (gram-equivalents per litre).	C.c. of *N*/10-potassium hydroxide for alteration of colour by one unit on colour standard.	Ratio.
0·0000*N*	0·002	1
0·0014*N*	0·008	4
0·01*N*	0·020	10
1·0*N*	1·0	500

Thus in practice, even with great care as in the first experiment of the table, the amount of alkali actually required to alter the colour of a phenolphthalein end-point is about fifty times the 0·0043 c.c. per 100 c.c. predicted for the absence of carbonate. The amount usually required is, of course, very much greater than this. It is evident that the amount of alkali required to produce this definite colour change, taken in conjunction with the established values for the hydrolysis of alkali carbonate, affords a ready and very delicate measure of the amount of carbonate present in a given solution. McCoy's value (*Amer. Chem. J.*, 1903, **29**, 437) for the alkalinity of *N*/10-sodium hydrogen carbonate is $2·9 \times 10^{-6} N - OH'$, which would be about standard No. 70; and Küster (*loc. cit.*) has pointed out that a very appreciable excess of carbonic acid is required for complete decolorisation.

The Best Depth of Colour for the End-point.

It will be noted that interpolations on the colour scale have been made use of above. This is based on the result of a series of titrations extending over the whole range of the scale up to No. 160. It appeared that not less than one-half as much alkali or acid was required to change the colour by a definite number of units in the neighbourhood of No. 150 than was required at No. 3. In other words, a definite amount of alkali causes the greatest colour-change in the least coloured solution; for example, if a given amount of alkali be required to change a colour from No. 3 to No. 6, the same amount would be required to change No. 150 to No. 156; but the change from No. 3 to No. 6 means doubling the intensity of colour, whilst the change from No. 150 to No. 156 is only 4 per cent., which is scarcely visible.

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* The potassium hydroxide was, however, freed from carbonate only by the addition of barium chloride, boiling, cooling, and decanting after some time and adding boiled-out sodium sulphate to remove the barium. Küster (*Zeitsch. anorg. Chem.*, 1897, **13**, 133) has shown that even Ostwald's method of preparation from metallic sodium and water does not exclude all carbon dioxide, and he describes an improvement on this method. He also points out the certainty of contamination from the air. Sodium hydroxide, purified by boiling in concentrated solution with quicklime, contained enough carbonate to give a value 0·006 c.c. in the table.

This shows that a pale colour in the neighbourhood of No. 3 is the most sensitive and therefore exact end-point to which to titrate. It possesses the further advantage of lying very appreciably nearer the theoretical point of neutrality.

The Influence of Carbon Dioxide on the Amount of Phenolphthalein necessary to develop Maximum Colour.

Whilst the next to the last section was merely an application of a commonplace of the theory of hydrolysis, it is not so obvious that the amount of phenolphthalein required depends on the concentration of carbonate intentionally or unintentionally present. The solution of phenolphthalein used throughout was a 1 per cent. solution in absolute alcohol, well boiled out, neutralised with alkali, and protected by a guard-tube of potassium hydroxide.

When carbon dioxide is excluded as thoroughly as possible (as in the first experiment of the table above), the colour deepens as phenolphthalein is added until 4 drops have been added to 100 c.c. of the solution being titrated. Increase of this amount to 10 or 20 drops causes no further change of colour. Hence it seems well invariably to use, say, 20 drops.

If, however, the carbonate present is $N/100$ or more, the depth of colour is roughly proportional to the amount of phenolphthalein added up to saturation with phenolphthalein (50—60 drops). This is an additional reason for invariably using 20 drops of phenolphthalein per 100 c.c.

The case of ordinary distilled water is particularly interesting, as apart from lack of delicacy, as shown above, the position of the end-point changes until just 20 drops of phenolphthalein have been added to each 100 c.c. of liquid; thus the error in the position of the end-point introduced by taking only 1 drop instead of the 20 drops amounts to 0·08 c.c. of $N/10$-potassium hydroxide; likewise by taking 4 drops instead of 20 drops the difference in amount of alkali required to produce a definite coloration is 0·03 c.c. of $N/10$-potassium hydroxide.

Attainable Accuracy of Acidimetric Titration.

If the simple precaution be taken in colouring the water in the titration flask to a pale tint comparable with that to be attained at the end-point, before adding the acid which is to be titrated, and if care be taken to avoid breathing in the direction of the solution, the result should always be reproducible within 0·1 per cent., apart from errors of calibration in the measuring vessel.

A glass-stoppered Erlenmeyer flask has but one drawback as a titrating vessel—that if the liquid is about 2·5 cm. deep, minute drops splash out through the neck when solution is added. This error may amount to 0·01 gram in adding 0·45 gram of strong alkali drop by drop, but it may be avoided by introducing into the flask a piece of glass longer than the diameter of the flask for the liquid being added to fall on.

0·01 Per cent. seems to be the limit of trustworthiness with which one may expect to duplicate a titration using large quantities of alkali and acid (say, 40 c.c. of *N*/5-solutions) when applying all known precautions, but not working in an atmosphere freed from carbon dioxide. The reproducibility of titration of a small quantity of alkali (for example, 0·45 gram of *N*/5-solution, or 35 c.c. of *N*/250-solution) may, however, be as great as 0·1 per cent.

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LXXXVI.—*The Absorption Spectra of Some Metallic Solutions.*

By SIR WALTER NOEL HARTLEY.

KONRAD SCHAEFER (*Zeitsch. wiss. Photochem.*, 1910, **8**, 212) has investigated the absorption spectra of nitrates following the method described in two papers which I had the honour of communicating to the Society (Trans., 1902, **81**, 556; 1903, **83**, 221). He confirms these observations in all particulars.

Schaefer examined solid potassium nitrate, and found the absorption band when the rays were transmitted through 0·37 mm. of the salt to be almost identical with that of the *N*/10-solution in water examined through 75 mm.*

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* I had previously examined thin layers of molten potassium nitrate, but found only a continuous absorption; it is obvious now that the film 0·5 mm. was too thick.

The selective absorption of the ultra-violet rays by the crystal proves that it is a property of the salt molecule, and is not indicative of any change in its constitution, such as might be caused by the formation of hydrates in aqueous solution by hydrolysis or by ionisation. Furthermore, it is evidence, as already established by experiments on ethyl nitrate (Trans., 1903, **83**, 234), and by Schaefer's more extended work, that the alkyl nitrates have a different structure, because under no conditions do they show any trace of an absorption band.

The following quotation from Schaefer's paper calls for some remark: "In cases where the general absorption caused by the metal is very slight, as, for instance, in solutions of the nitrates of lithium, sodium, potassium, strontium, and barium, the complete identity of the NO_3 absorption was established, notwithstanding that here the atomic masses of the metals, which according to Hartley should influence the vibratory motion of the NO_3 group, exhibit marked differences. The relative differences in the atomic masses, which alone can enter into the question, are here, in fact, greater than in the groups KNO_3, $AgNO_3$, $TlNO_3$, to which Hartley refers."

The author has not established any new fact affecting the *solutions*, and his criticism here appears to be based on an error or misunderstanding of the argument advanced, because in the original communication it is expressly stated that in a salt MNO_3, where M represents the metal, the velocity of motion of M may be accelerated or retarded by the NO_3 or vice versa, the rate of vibration being determined by the relative masses of the ions; we are dealing in fact with equivalent weights.

When the mass of the positive ion is H = 1, K = 39·15, Ag = 107·93, Tl = 204·1, and so on, we have $NO_3 = 62$; but for $NO_3 = 62$, we have Cd = 56, Th = 58, and Pb = 103·3, from which it may be seen how much greater the relative or equivalent masses of Ag, Tl, and Pb are than that of NO_3. Similarly, the differences in the equivalent weights of the metals Zn = 32·5, Mg = 12, Ca = 20, Sr = 43·5, Ba = 68·5, and of the group $NO_3 = 62$, are too small to have any appreciable effect on the absorption spectra, especially as the bases exert little absorption, if any at all, in the region of wave-lengths usually photographed.

Schaefer further states that silver and thallium each exert a general absorption peculiar to the metal, which accounts for the differences in the absorption spectra of their nitrates, and that the difference is proportional to the combination of the metal in the undissociated molecule.

This statement is quite in accord with my observations and with the conclusion that the absorption spectra are due to the nitrate molecule in each case, whether as nitric acid or a metallic nitrate, that the salt molecule is not necessarily dissociated, and that the increased general absorption observed in solutions of these salts is accounted for by the high values of the atomic weights of the metallic elements. The question which arises, however, is: Does the general absorption caused by these elements extend so far down into the less refrangible rays as to interfere with or modify the absorption bands belonging to the NO_3 group as observed in dilute solutions? In the case of thorium and erbium salts, which were the subject of experiments, the answer was in the negative, but the measurements of the erbium and thorium chlorides were not quoted (Trans., 1903, **83**, 221).

No independent examination of the absorption spectra of any pure salts of the elements in question appears to have been made other than of the nitrates, and I have therefore reinvestigated salts of thorium, thallium, silver, and lead, and have tabulated the results.

This course has been deemed advisable because Schaefer examined *mixtures* of sodium nitrate with sulphates of other metals, and drew deductions from the absorption curves of such mixtures instead of comparing solutions containing equivalent quantities of the pure salts. Solutions of thallous nitrate and silver nitrate do not conform to Beer's law, as Schaefer observes, strong solutions showing a proportionately greater absorption.

The absorption spectra of silver are particularly interesting, as may be seen on reference to Trans., 1902, **81**, 572, where nitric acid, potassium nitrate, and silver nitrate are compared.

It is necessary here to quote only the figures derived from solutions of the latter salt, and compare them with solutions of silver sulphate.

Silver Nitrate.

Layer of liquid. mm.	Concentration.	Spectrum continuous $^1/\lambda$.	Absorption band.	Rays transmitted
10	normal	to 3004		
10	,,	3002	$^1/\lambda$. $^1/\lambda$.	$^1/\lambda$.
5	,,	3069	**3069** to **3535**	to 3706
4	,,	3069	**3069** to **3540**	3652
4	,,	3067	**3069** to **3530**	3638
200	*N*/20	3069		
200	*N*/20	3067		
200	*N*/40	3069	**3069** to **3579**	to 3900
200	*N*/50	3148	**3148** to **3579**	3900
200	*N*/50	3150	**3150** to **3531**	3888
200	*N*/200	3149	**8149** to **3504**	3940

Silver Sulphate, 107·9 grams of Ag per 40 litres.

200 mm. *N*/40 Spectrum continuous to......... $^1/\lambda$ 4008

The significance of these figures becomes apparent when it is understood that 10 mm. of a normal solution are equivalent to 200 mm. of $N/20$-solution; 5 mm. to 200 mm. of $N/40$, and 4 mm. to 200 mm. of $N/50$. In the case of nitric acid and potassium nitrate, the two series of solutions yielded spectra which were identical. In the case of silver nitrate it will be seen that the measurements of the normal solutions differ from those which are more dilute photographed through equivalent thicknesses.

This indicates a change in the constitution of the solution. If now we compare these measurements with those of the spectra of silver sulphate, we see that the transmitted rays in the absorption spectrum of the latter salt extend beyond those of the silver nitrate of the same concentration, hence the specific absorption exerted by the silver does not limit the extent of the rays of the spectrum absorbed or transmitted by the silver nitrate solution.

Thallium Nitrate.

Layer of liquid. mm.	Concentration.	Spectrum continuous $^1/\lambda$.	Absorption band. $^1/\lambda$. $^1/\lambda$.	Rays transmitted $^1/\lambda$.
10	$N/4$	to 3080	**3080 to 3647**	to 3896
8	$N/4$	3080	**3080 to 3647**	3896
4	$N/4$	3080	**3080 to 3647**	3896
5	$N/10$	Spectrum continuous to	......	3896
4	$N/10$	,, ,, ,,	......	4028
2	$N/10$	,, ,, ,,	......	4055

Thallium Sulphate, 204·1 grams of Tl per 20 litres.

200	$N/20$	Spectrum continuous to	......	3896
2	$N/20$	,, ,, ,,	......	4220

On examining these figures we find that 50, 40, and 20 mm. of the $N/20$-solution of thallium sulphate are equivalent to 10, 8, and 4 mm. of the $N/4$-solution of thallium nitrate, and that the three different thicknesses of the latter solution transmit exactly the same spectrum. Thallium sulphate is a sparingly soluble salt, hence the strength of the solution is $N/20$; but it will be seen from 200 mm. down to 2 mm. the rays transmitted range from $^1/\lambda$ 3890 to 4220. The thickness of 200 mm. is ten times as great as the equivalent of $N/4$-solution, and twenty times as great as the 5 mm. of the $N/10$-solution; yet it transmits the rays freely.

Lead Nitrate.

Layer of liquid. mm.	Concentration.	Spectrum continuous $^1/\lambda$.	Absorption band. $^1/\lambda$. $^1/\lambda$.	Rays transmitted. $^1/\lambda$.
15	*N*/2	to 3062		
10	*N*/2	3148 feebly	**3148 to 3760**	to 3836
5	*N*/2	3148	**3148 to 3760**	3836
4	*N*/2	3272 feebly	**3274 to 3535**	3894
200	*N*/20	3021		
200	*N*/70	3075		
200	*N*/80	3075	**3285 to 3537**	to 3674
200	*N*/90	3075	**3075 to 3550**	3915

Lead Acetate, 103·4 grams of Pb per 20 litres.

200	*N*/20	Spectrum continuous to	3760
2	*N*/20	,, ,, ,, ...	3984

The sparingly soluble lead salts do not admit of normal solutions being prepared, but it will be seen above that 200 mm. of *N*/20-lead acetate solution transmits continuous rays beyond those transmitted by 200 mm. of *N*/20-lead nitrate solution.

Solution of Thorium Nitrate, $Th(NO_3)_4,12H_2O$.

Normal solution = 62 grams of NO_3 and 58 grams of Th per litre.

Solution of Thorium Chloride of exactly the same concentration, that is, 58 grams of Th per litre.

The Nitrate.

Thicknesses of layer of liquid. mm.	Rays transmitted. $^1/\lambda$.
200	2787
100	2877
50	2980
30	3002
15	3065
2	Absorption band **3354 to 3510** Rays transmitted 3510 to 3960

The Chloride.

Thicknesses of layer of liquid. mm.	Rays transmitted. $^1/\lambda$.
200	3043
100	3638
50	3638
40	3761
30	3825
20	3886
15	4115
10	4321
5	4368
4	4413

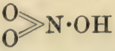
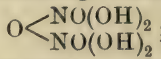
Comparing the absorption of rays exerted by the thorium nitrate with that of the thorium chloride in solutions of the same concentration, it will be seen that the chloride through 200 mm. shows no band at any thickness down to 30 mm.; and it transmits a continuous spectrum extending beyond the band of absorption exerted by thorium nitrate and nitrates generally through only 2 mm.; from which it is evident that the thorium alone by its specific absorption does not limit or obscure the absorption exerted by the nitrate.

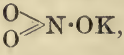
The sparing solubility of thallium and silver sulphates, and of lead acetate necessitates the examination of more dilute solutions than those of their nitrates, but similar evidence leads to the same conclusion, namely, that no metal of the group, thallium, silver, and lead, by its specific absorption, obscures or interferes with the absorption spectrum of its nitrate, notwithstanding that each of them, like the metal thorium, shows a distinctive general absorption.

Schaefer states "the differences in the absorption spectra of inorganic nitrates, which Hartley first found, have been confirmed. Nevertheless, I cannot agree with the conclusions which Hartley drew from them." He believes that the cause of the differences observed in some of the absorption curves is more chemical than physical in its origin. In this connexion I have particularly described the chemical action of light on some of the solutions. The action was evidently preceded by hydrolysis, and it eventually led to the precipitation of hydrated peroxides of cobalt and of manganese. Likewise, thorium nitrate and chloride formed precipitates of basic salts. Similarly also, basic compounds were deposited from bismuth and lead nitrates. In such cases there is, of course, the formation of free acid.

In connexion with this subject it is necessary to refer to the work of Ernst Müller (*Ann. Physik*, 1906, [iv], **21**, 515). He determined the absorption power over a considerable part of the spectrum, of copper sulphate, nickel sulphate, potassium chromate, and cupric chloride solutions. He found it impossible to explain the colour changes which accompany dilution on the basis of dissociation alone; other factors which must be taken into account are the formation and decomposition of hydrates and complex molecules or ions. The colour of a dilute solution cannot under the influence of heat be made to correspond exactly with the colour of a cold concentrated solution.

It appears to be probable that small differences in the absorption curves of the spectra of solutions of nitrates in which the metal exerts no marked general absorption, may be explained by what has already been proved, namely, that many nitrates are hydrated in solution, others are hydrolysed, and the nitric acid then becomes hydrated (Trans., 1903, **83**, 658, and Notes on the Constitution of Nitric Acid and Hydrates, *Sci. Proc. Roy. Dublin Soc.*, 1905, **10**, (N.S.), 373).

H. Erdmann isolated, crystallised, and examined the properties of five differently constituted nitric acids, four of which were discovered by Graham and one by Pickering, namely, metanitric acid,  $\begin{smallmatrix}O\\O\end{smallmatrix}\!\!>\!N\cdot OH$; tetrabasic nitric acid,  $O\!<\!\begin{smallmatrix}NO(OH)_2\\NO(OH)_2\end{smallmatrix}$; tribasic acid, $O\!:\!N(OH)_3$; octabasic acid, $(HO)_4N\cdot O\cdot N(OH)_4$; and the ortho-acid, $N(OH)_5$.

Schaefer's experiment on solid potassium nitrate is a proof that neither ionisation nor hydrolysis is the cause of the appearance of the absorption band. Moreover, it is convincing evidence that the absorption spectrum of the solid salt is a property of the undissociated salt molecule, KNO_3. At the same time, it is not incompatible with the hypothesis that the compound is in a condition of molecular strain, which may be due to the existence of unsaturated affinities in the compound. It may be presumed that it exists as a metanitrate,  $\begin{smallmatrix}O\\O\end{smallmatrix}\!\!>\!N\cdot OK$, with the possibility of forming a tribasic compound, $O\!:\!N\cdot OK(OH)_2$, or a pentabasic salt, $O\!:\!N\cdot OK(OH)_4$, which is derived from the ortho-acid, $O\!:\!N(OH)_5$.

LXXXVII.—*The Absorption Spectra of Permanganates.*

By SIR WALTER NOEL HARTLEY.

IN connexion with the hydrolysis of complex molecules of salts and the subsequent chemical changes which are increased or accelerated by light, I may refer to the experiments of Mr. J. E. Purvis on "The influence of dilution on the colour and the absorption spectra of various permanganates" (*Proc. Camb. Phil. Soc.*, 1909, **15**, 111).

Experiments were made on potassium, zinc, and barium permanganates containing in 1000 c.c. of distilled water 0·316, 0·262, and 0·375 gram of the respective salts. They were each examined through cells 5 mm., 154 mm., and 310 mm. thick, each solution containing the same quantity of permanganate, the comparative solutions being made by diluting the strongest one 30·8 and 62 times respectively. The five bands measured by Lecocq de Boisbaudran were photographed, and the paper is illustrated by excellent photographic reproductions of the spectra, which show with distinctness only three of the bands.

"The explanation which seems to account for the changes is that the dissociating force of the water slowly acted on the dissolved permanganates, so that the ionic condition of $\overset{+}{R}$ and $\overset{-}{MnO_4}$, where $\overset{+}{R}$ represents the metallic ion, broke down. One may imagine that the $\overset{-}{MnO_4}$ ion undergoes further dissociation into MnO_3 and O, or into MnO_2 and O_2. In such dilute solutions the tension between the molecules of water surrounding the ions must have been very considerable, and it may have been so great as to destroy the MnO_4 condition, so that further changes took place which became visible in changes of colour, in changes in the width of the bands, and in the liberation of oxygen; and these changes would be accelerated by the vibrations of light."

"The intermediate stages of the changes might be represented by the narrowing of the bands 1, 2, and 3, and the widening of the bands 4 and 5, and these might correspond to changes of the MnO_4 ions into MnO_3 and O ions."

Such is the author's view. I venture to suggest that a simpler explanation is that which I have given in the case of nitrates which form basic salts, and in particular thorium nitrate (Trans., 1903, **83**, 221). A similar change also occurs in manganese nitrate and, as I shall show, in manganese sulphate.

In dilute solution the permanganates are hydrolysed and then decomposed into a colloidal solution of manganic hydroxide, $MnO(OH)_2$, and free oxygen. This action occurs even when the solutions are made in darkness and preserved in the dark. The most striking change seen in the spectra is a greatly increased general absorption, that is, a shortening of the transmitted rays. With solutions preserved in darkness it is apparently proportional to the dilution, but the effect of sunlight greatly increases the decomposition. The narrowing of the bands λλ 546 and 524, and the widening of those at λλ 504, 486, are easily explained by the decomposition having diminished the quantity of the permanganate or permanganic acid, and therefore weakened the bands and increased the quantity of the hydroxide, $MnO(OH)_2$, in colloidal solution; this has greatly extended the general absorption until it in part overlies the more refrangible of the bands. The absorption bands of permanganates are not characterised by sharpness; they have a hazy indistinctness, with no definite boundary lines such as are commonly seen in uranium, didymium, and erbium absorption spectra.

Owing to these properties, if the light is not diminished in intensity but the permanganate is reduced in quantity, the intensity of the bands will be diminished, and this will cause a reduction in their width. If, however, the intensity of the transmitted light is diminished, the reverse effect will be seen in an increased width of the bands. The intensity of the light is not diminished so far down into the green as λ 524, but the colloidal solution of the hydroxide, $MnO(OH)_2$, not only extends the complete absorption in the direction of the bands, but also enfeebles the transmitted rays by a partial absorption extending to λ 504.

Hence, two of the bands in the less refrangible rays are narrower, and two in the more refrangible rays are broader, than in the unaltered solutions.

The observation is recorded that the stronger solutions appear to have the bands shifted towards the red, and this shift appeared to decrease with increased refrangibility of the absorbed rays. "In order to explain the different positions of the bands of the different solutions, the observations of H. Becquerel (*Compt. rend.*, 1886, **102**, 106) show that such differences depend upon the concentration; the greater the concentration, the greater the shift of the bands towards the red end of the spectrum." This appears to offer no explanation of the cause of the shifting. If, however, we state that the concentrated solution is mainly a solution of the salt, and that dilution causes hydrolysis, the shift of the edge of the band to a more refrangible group of rays is precisely what might be expected by the conversion of barium permanganate into hydrogen permanganate; furthermore, we should expect the shift be of greater extent in the case of the barium salt than in that of the zinc permanganate, and from an inspection of the photographs this appears to be the case. Measurements were not made by Purvis; the figures are taken from Lecocq de Boisbaudran's "Spectres Lumineux." From the very nature of the bands they could not be measured with the precision desirable even with the dispersion of calcite prisms, owing to their indefinite character. This can be seen by comparing the photographs taken by Purvis No. 8 with No. 5; the former appears to be stronger than the latter, the bands being broader and more distinct, though they both represent solutions of the same salt of the same concentration, prepared and kept in darkness.

Manganese Sulphate.—Similar observations were made on this salt. A quantity of 4 kilograms was prepared in the highest degree of purity; it contained no trace of any other metallic base, and was perfectly neutral. The colour of the crystals was a delicate pale pink; a normal solution made with distilled water had a similar colour. The solution kept in a stoppered bottle passed through the following changes in colour on keeping. The pink became paler, the solution then became colourless, the colourless solution gradually assumed a pale yellow, the yellow gradually deepened to an amber tint. The disappearance of the pale pink was caused by the pale yellow, at first neutralising the violet and blue rays, which being the complementary colours were freely transmitted; the unabsorbed green rays neutralise the red, thus constituting a colourless solution.

When the green rays had overpowered the pink, the yellow began to be visible. It must be borne in mind that the absorption phenomena are complicated by the admixture of an excess of white light, but this colour-change constantly occurs in pure solutions of the salt. In the original solution a narrow and well-defined absorption-band was photographed, which became obscured, and disappeared as the yellow colour developed; and this eventually became of a pale brown tint. For the explanation of the colour-changes we must admit that hydrolysis and oxidation are producing the colloidal hydroxide, $MnO(OH)_2$. I have recorded the similar change in a normal solution of manganese nitrate, which led to the formation of a brown precipitate of manganic hydroxide.

The Absorption Band.—A normal solution of the salt, $MnSO_4,5H_2O$, was examined through a column of liquid 200 mm. long. A general absorption enfeebles the rays as far as λ 3860, with a total absorption approximately as far as λ 3290; a transient absorption band lies between a broad air-line, λ 4025·3, and another air-line, very sharp and strong, λ 3995; there is a feeble extension of the band to λ 3952. The band overlaps a sharp lead-line, λ 4019·8, but only weakens without obscuring it. The absorption is therefore but feeble, and it is apparently caused by the oxidation of the solution. It indicates the progress of a chemical reaction, and the band disappears when the reaction is complete.

Note.—Since the foregoing observations were prepared for publication in February, 1911, a paper by T. R. Merton (Trans., 1911, **99**, 637) has appeared with almost the same title.

It records careful measurements of the most conspicuous absorption bands in solutions of various permanganates in different liquids, including a solid solution of potassium permanganate in potassium perchlorate. The measurements of the maxima of absorption only are given, and all description of the nature of the bands as seen in the different solvents has unfortunately been omitted. Nevertheless, the author's conclusion is quite justified in respect to the general nature of the absorption being due to the atomic grouping, MnO_4, which is influenced very little by the cation or by the extent of dissociation of the salt.

A very remarkable difference, however, is to be observed between the measurements of the bands in the solid solution and those in the liquids, which leads to a question whether they are the same bands shifted towards the violet end of the spectrum.

Having made a careful comparison of the figures, I have arrived at the conclusion that the bands in the solid solution are shifted into a region of less refrangible rays when the potassium permanganate is dissolved. This is highly suggestive of a state of combination of the solute with the solvent.

The following arrangement of the figures explains this. Let the solid solution and the solvents be numbered 1 to 11, and the bands be indicated in the order of the magnitude of the wave-lengths of the obscured rays by the letters *A*, *B*, *C*, selecting in every case the spectrum of potassium permanganate. By ascertaining the differences between the bands *A* and *B* and between *B* and *C* respectively in different solutions, the effect of the solvent is clearly shown, the probable accuracy of the figures being accepted as ± 3 Ångströms.

	A.	*B.*	*C.*	Differences.	
(1) Solid solution	5577	5345	5135	232	210 Å
(2) Solution in acetone............	5735	5496	5276	239	220
(3) ,, acetic anhydride	5719	5480	5260	239	220
(4) ,, acetonitrile	5718	5478	5258	240	220
(5) ,, methyl acetate...	5720	5480	5258	240	222
(6) ,, ,, alcohol..	5747	5505	5285	242	220
(7) ,, ethyl ,, ..	5747	5503	5282	244	221
(8) ,, ,, and amyl alcohol	5747	5504	5280	243	224
(9) ,, ethylene glycol.	5730	5484	5267	246	217
(10) ,, water	5719	5477	5256	242	221
(11) ,, pyridine	5738	5490	5271	248	219

It will be observed that the bands *A*, *B*, and *C* of No. 1, the solid solution, differ widely in position from the three corresponding bands in all the other solutions, although all these agree fairly well; the difference between No. 1 and all the other numbers

for the band *A*, lies between 142 and 172 Å
,, ,, *B*, ,, ,, 132 ,, 160
,, ,, *C*, ,, ,, 121 ,, 150

The question arises whether the bands of No. 1 are really the bands corresponding to *A*, *B*, and *C* in the liquids, or whether they are not three more refrangible bands. This can be solved by the differences, for in the latter case the band *A* of No. 1 would correspond with band *B* of No. 2, etc., and the difference between *A* and *B* in the former would correspond with the difference between *B* and *C* in the latter, but it does not; it follows, therefore, that the action of the solvent on the solid solute changes the position of the bands into a region where the absorbed rays are of less refrangibility by 121 to 170 Ångströms, according to whether the band is *A*, *B*, or *C*.

As the author has remarked, it appears to be independent of the optical properties of the solvent.

LXXXVIII.—*The Rate of Reduction of Carbon Dioxide by Carbon.*

By THOMAS FRED ERIC RHEAD and RICHARD VERNON WHEELER.

IN previous communications (Trans., 1910, **97**, 2178; 1911, **99**, 1140) we have, following the work of Boudouard, Schenck and Zimmermann, and Smitz and Wolff referred to therein, given the results of experiments made to determine the effect of temperature and pressure on the equilibrium $2CO \rightleftharpoons CO_2 + C$; and we have shown that, whilst equilibrium is reached fairly rapidly from either side at temperatures above 1000°, below 800° the rates of reaction are very slow indeed.

The United States Bureau of Mines has recently issued a pamphlet (Bulletin No. 7, 1911) entitled, "Essential factors in the formation of producer gas," by J. C. Clement, L. H. Adams, and C. N. Hoskins, in which a series of experiments on the rate of formation of carbon monoxide at high temperatures is described. These experiments are stated to have had as their object "a critical repetition of Boudouard's experiments" (on the equilibrium $2CO \rightleftharpoons CO_2 + C$), "and a continuation of them at higher temperatures." The method of experiment employed was to pass carbon dioxide in a continuous stream at different speeds through charcoal packed in a porcelain tube, and heated in an electric resistance furnace at different temperatures. It was found, as might be expected, that the amount of carbon dioxide reduced at any given temperature during its passage through the heated charcoal depended on the speed at which it was passed; and that the difference between the effect of a slow and a rapid stream was more marked at low than at high temperatures. From the experimental data obtained regarding the percentage of carbon monoxide formed when different speeds of passage of the carbon dioxide were employed at any given temperature, an attempt is made to calculate what should be the percentage for a speed *nil*. This is then regarded as being the percentage *in equilibrium* with carbon dioxide and carbon at the temperature employed. That such an assumption is quite inadmissible is evident from a comparison between the results obtained by such calculations and our own, where the gases were maintained in contact with the heated carbon for, in some cases, several days before equilibrium was established. The longest time of contact in Clement, Adams, and Hoskins' experiments was 188·6 seconds. This was with the carbon at a temperature of 800°, when 50·3 per cent. of carbon monoxide appeared in the products, and it is assumed that an "infinite" time of contact would merely increase the percentage of carbon monoxide formed to 52·6.

Their results, with our own for comparison, are as follow:

Temperature.	Carbon monoxide in equilibrium with carbon dioxide. Per cent. by volume. Clement, Adams, and Hoskins.	 Rhead and Wheeler.
800°	52·6	86·4
850	73·8	93·2
900	87·1	96·6
925	91·2	97·5
1000	93·9	99·4
1100	97·1	99·8

The method of experiment employed by Clement, Adams, and Hoskins, although it yields results of no value from the point of view of determining the quantities of carbon monoxide and dioxide in equilibrium over carbon at different temperatures, should afford some information regarding the effect of temperature on the speed of the reaction $CO_2 + C \longrightarrow 2CO$.

By interpolation from the experimental numbers given, we have calculated that for "times of contact"* of 2·5, 5, 7·5, and 10 seconds the following quantities of carbon dioxide were reduced by the carbon at different temperatures:

Carbon Dioxide Reduced, per cent. of Original Volume.

	Time of contact (seconds).			
Temperature.	2·5.	5·0.	7·5.	10·0.
800°	3·1	5·8	8·7	10·5
850	—	16·3	21·6	30·8
900	22·7	36·0	46·0	54·4
1000	66·7	73·9	81·0	85·2
1100	92·3	96·1	96·5	96·8

Curves obtained by plotting the percentages of carbon dioxide as a function of temperature give a very fair idea of the rapidity with which the rate of reduction falls off as the temperature of the carbon is decreased (Fig. 2). We will refer to these curves again when considering our own results.

The object of the present investigation, which was begun by one of us in 1906 and forms part of a research on the mode of combustion of carbon, was to determine the rate at which carbon dioxide is reduced by carbon at different temperatures, for comparison with similar determinations of the rates at which oxygen combines with (1) carbon, and (2) carbon monoxide, under the same conditions of experiment.

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* The calculation of the "time of contact" involves certain arbitrary assumptions regarding the amount of air space in the packed reaction-tube, and is rendered still more hypothetical by the fact that the volume of carbon dioxide that enters the reaction-tube is not the same as the volume of the gases (carbon dioxide and monoxide) that leaves.

We have already shown (Trans., 1911, **99**, 1145) that carbon dioxide should, theoretically, be reduced by carbon at a temperature of 315° or less, but that the *rate* at which reduction takes place is extremely slow even at 700°. We are now able to give the relative rates of reduction, under given conditions of experiment, at temperatures of 750° and 1100°, and at intermediate temperatures of 50° interval. From the data thus obtained the rates at lower temperatures can be calculated.

In the method of experiment that we have employed, use is made of the fact that the reaction is accompanied by a change of volume, and that, therefore, if the reaction takes place in a closed system, its progress can be directly measured by the change of pressure. Starting with an initial concentration of 100 per cent. carbon dioxide, or, in one series of experiments, with a mixture of carbon dioxide with nitrogen containing 20 per cent. of the former, the gases were circulated continuously in a closed system, so that they passed at a known speed through purified carbon contained in a porcelain tube which was heated by means of an electric resistance furnace. The pressure of the gases in the system was recorded at regular intervals of time from the readings of a mercury manometer. The apparatus is described in detail in the experimental part of this paper.

Since the reaction between carbon dioxide and carbon is reversible, the question arises whether the reverse reaction $2CO \longrightarrow CO_2 + C$ affects in any way determinations of the velocity of the reaction $CO_2 + C \dashrightarrow 2CO$. We have shown (Trans., 1910, **97**, 2189) that at 850° the reduction of carbon dioxide takes place at a speed one hundred and sixty-six times as great as the dissociation of carbon monoxide under the same experimental conditions. There is no reason for believing that the ratio between the rates of the two reactions (166 : 1) suffers any material alteration at temperatures below 850°. Moreover, at this temperature only 6·23 per cent. of carbon dioxide remains in equilibrium with carbon monoxide and carbon at atmospheric pressure, and at higher temperatures the equilibrium is still further displaced in the direction of the carbon monoxide, so that the expression for the velocity of reaction:

$$k(C_2{}^{n_2} . C'_2{}^{n'_2} \ldots\ldots\ldots - kC_1{}^{n_1} . C'_1{}^{n'_1} \ldots\ldots) \text{ (van't Hoff)},$$

for changes that lead to a state of equilibrium, may be simplified for the case when equilibrium means the complete predominance of one of the two systems. The expression then becomes $kC^nC'^{n'}$, and since we are concerned with the concentration of the carbon dioxide only, the relation $1/t \log C_o/C_t$, derived for a unimolecular reaction from the above expression, can be employed for determining the relative velocities at different temperatures.

Our results can be summarised shortly as follows:

The velocity of reaction increases with increase of temperature, the mean velocity ratios for a temperature interval of 10° diminishing fairly regularly as the temperature scale is ascended; thus, in the series of experiments in which a mixture containing 20 per cent. of carbon dioxide and 80 per cent. of nitrogen was employed, the following mean values of k at different temperatures were found:

Temperature.	k ($t=1$ minute).
900°	0·00060
950	0·00374
1000	0·01764
1050	0·05760
1100	0·10570

The mean velocity ratio for an interval of 10°, obtained from the expression $k_{t+10}/k_t = 10^{10b}$, are given in the table that follows, together with the values of b obtained from the experimental numbers.

Temperature range.	b.	k_{t+10}/k_t.
900— 950°	0·01589	1·44
950—1000	0·01346	1·36
1000—1050	0·01028	1·27
1050—1100	0·00527	1·13

Assuming that the ratio k_{t+10}/k_t decreases regularly for every 50° decrease in temperature by 0·10 (the mean difference over the range 900—1100°), the values of k and the percentages of carbon dioxide reduced after sixty minutes' circulation are calculated as follows:

Temperature.	k ($t=1$ minute),	Carbon dioxide reduced after 60 minutes (per cent.).
850°	0·00006942	0·9545
800	0·000005855	0·0808
750	0·0000003673	0·0051
700	0·00000001742	0·0002

The values of k and the percentages of carbon dioxide reduced in a given time are, of course, only relative, and are determined by the conditions of experiment as regards rate of circulation of the gases and the length of the column of carbon. The results are of most value in connexion with the question of the mode of combustion of carbon by oxygen; for it is obvious that if under the same conditions of experiment an appreciable quantity of carbon monoxide is found in the products of combustion of carbon by air at, say, 400°, that carbon monoxide cannot have arisen from the reduction of carbon dioxide.

EXPERIMENTAL.

The "circulation" apparatus that we have employed for the present investigation, as well as for the determination of the rates

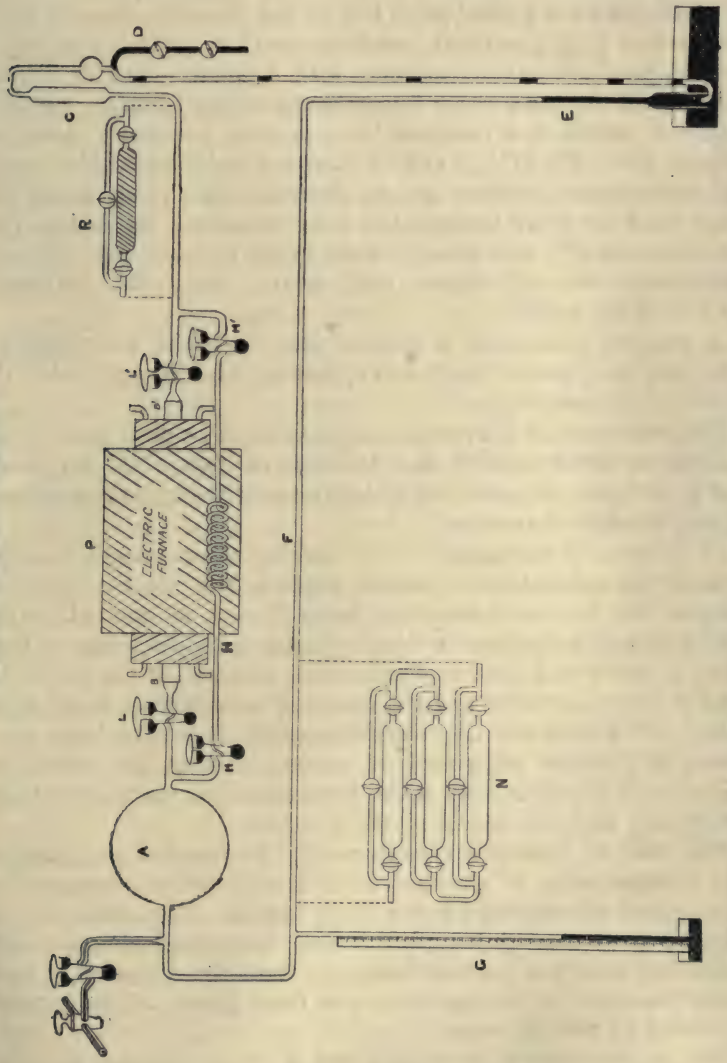

Fig. 1.—*Circulation apparatus.*

The portion of the apparatus R *was not used for the experiments described in this paper.*

of oxidation of carbon and of carbon monoxide recorded in a subsequent paper, is similar to that already described and figured in our paper on the influence of temperature on the equilibrium

$2CO \rightleftharpoons CO_2 + C$. Certain alterations in detail, however, which are of importance as regards the relative value of the results obtained for the velocities of these three reactions, make it necessary to describe the apparatus here.

The glass globe *A* (Fig. 1) serves as a reservoir for the gases. It is connected by a ground joint *B* with the porcelain tube in which the carbon (highly-purified wood charcoal) is packed. A similar ground joint *B′* makes connexion with a calcium chloride drying-tube *C* and the head of an automatically-acting Sprengel mercury-pump *D*, which is a modified form of that previously described (Trans., 1910, **97**, 2178),* and by means of which circulation under the atmospheric pressure can be effected. This pump draws the gases from the globe through the tube containing the carbon (the "reaction-tube"), and delivers them under mercury into the wide manometric tube *E*, whence they return, along the horizontal tube *F*, to the globe.

A mercury manometer *G* is fixed near the globe, and serves for observing the pressure inside the apparatus, and thus following the course of the reaction.

The reaction-tube is by-passed by the tube *H*, a glass spiral being inserted to avoid rigidity, so that when the taps *L*, *L′* are closed, and *M*, *M′* open, the gases can be drawn round the apparatus without passing through the carbon.

It is often of advantage to be able to obtain samples of the gases in the apparatus at different stages in the reaction. For this purpose the by-passed sampling tubes *N* can be inserted in the circuit at any convenient point (preferably near the globe, as indicated by the dotted lines in the diagram, a portion of the horizontal tube *F* being cut away and the sampling arrangement fused in its place). It will be seen that the arrangement of taps on these tubes allows of a sample being shut off without altering the pressure of the gases in the main body of the apparatus, and therefore without interfering with the course of the reaction.

The electric resistance tube-furnace *P* is wound with platinum, the winding being so arranged as to give a uniform temperature throughout the middle 13 cm. of its length. The ends of the furnace carry water-jackets, which keep the ground glass-porcelain joints cool and thus prevent leakage. With the exception of these joints the whole of the apparatus is of fused glass. All the taps are protected by mercury-cups.

The reaction-tube is 26 cm. long and of 1·2 cm. internal diameter. The purified carbon, weighing just under 3 grams and sieved through a 10- and on a 30-mesh sieve so as to be of uniform size, occupies the middle 9 cm. only, being kept in position by plugs of small-bore quartz tubing which just slide into the porcelain tube.

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* See also "The combination of hydrogen and oxygen in contact with hot surfaces," Bone and Wheeler, *Phil. Trans.*, 1906, *A*, **206**, 1.

Temperatures are read by means of a platinum and platinum-rhodium thermo-couple which passes between the furnace-tube and the reaction-tube, the junction being at the centre of the uniformly heated portion; and are recorded on a Cambridge Scientific Instrument Company's Thread-Recorder.

Method of Conducting an Experiment.—The whole apparatus, including the reaction-tube, having been thoroughly exhausted at room temperature, the temperature of the furnace was raised to 1100°, and the reaction-tube containing the carbon further exhausted at this temperature, taps *L* and *M* being closed. This operation removed from the carbon gases unextractable at the ordinary temperature, and ensured that the reacting surface was in a similar condition prior to each experiment—a matter of supreme importance in the determination of the relative velocities of gas reactions.

The temperature of the furnace was then brought to the experimental temperature, and maintained constant by means of the device described in previous papers (*loc. cit.*, **97**, 2185; **99**, 1149).

Taps *L*, *L′* having been closed and *M*, *M′* opened, pure carbon dioxide was passed into the apparatus. Since for every volume of carbon dioxide reduced two volumes of carbon monoxide are formed, it was necessary to allow for the doubling of the pressure inside the apparatus. The initial pressure of the carbon dioxide could not, therefore, be more than 380 mm. For the sake of uniformity in the rate of circulation of the gases throughout each experiment, it was found best, however, not to start with a pressure of carbon dioxide greater than about 300 mm.; for although the automatic Sprengel pump employed was capable of circulating gases at atmospheric pressure, it was found that the rate of circulation could not be relied on to remain constant after the pressure in the apparatus had increased much above 600 mm. There was no appreciable variation in the rate of circulation as the pressure increased from 200 mm. to 600 mm.

The carbon dioxide gas used was, in the majority of the experiments, obtained from the solid, being allowed to evaporate slowly from a vacuum-jacketted tube directly into the vacuous apparatus. It was there allowed to circulate during twelve hours through the by-pass of the reaction-tube, being thus dried by the calcium-chloride tube in the circuit. The rate of circulation was then adjusted by regulating the taps on the Sprengel pump.

To start an experiment, all that was necessary was to close taps

M, *M′* and open *L*, *L′* quickly, thus admitting the gas to the previously vacuous reaction-tube. A few minutes were allowed to elapse before taking the first reading of the manometer in order to ensure that the pressure throughout the apparatus had been equalised. Readings of the manometer were then taken at regular intervals of time, simultaneous readings of the barometric pressure and the room temperature being made.

To stop an experiment, taps *L*, *L′* were closed simultaneously, and the whole of the gases on the pump side of the reaction-tube transferred to the globe, where they were allowed to remain for two or three hours. A sample was then withdrawn for analysis.

Since, as stated above, a few minutes were allowed to elapse before the first pressure reading was taken, a certain amount of reduction of the carbon dioxide would have already taken place in that time. The partial pressure of the carbon dioxide at time 0 has therefore been calculated in each experiment from the analysis of the final gases. These were never found to contain any hydrogen, nor more than 0·2 per cent. of nitrogen, showing that the drying of the gases was efficient, and that the apparatus had remained satisfactorily gas-tight.

Results of Experiments.—We have made several series of experiments at different temperatures, using a different time of circulation of the gases in each series. By "time of circulation" we mean the time taken for the whole of the contents of the apparatus to be drawn once through the reaction-tube. This was determined, both before and after each experiment, by recording the time taken by the circulation-pump in delivering a measured quantity of gas (100 c.c.) into a collecting vessel.

The percentage of the total volume of carbon dioxide contained in the apparatus that undergoes reduction per unit of time depends directly, of course, on the time of circulation. For the shorter the time of circulation the oftener are the contents of the reaction-tube changed and the greater is the number of carbon dioxide molecules brought into contact with the carbon per unit of time. It need hardly be pointed out that the *relative* rates of reduction observed at different temperatures when the time of circulation is, say, forty minutes, should not differ to any marked extent from the *relative* rates at different temperatures observed in another series in which the time of circulation is twenty minutes. It is necessary, however, that the time of circulation should be sufficiently rapid to ensure that at the highest temperatures of the series the contents of the reaction-tube are changed before equilibrium can be established; for, unless there is always an excess of carbon dioxide in contact with the carbon, too low a rate of reduction will be observed.

To avoid error from this cause, the relative rates of reduction at different temperatures have been determined with times of circulation of forty, twenty, twelve, and five minutes. Of the series in which pure carbon dioxide was employed, all of which showed the same characteristics, only two, with times of circulation of forty and twelve minutes respectively, need be detailed.

In the tables that follow are given, in separate columns:

(1) t, the time in minutes.

(2) P_{CO_2}, the partial pressure of the carbon dioxide, calculated from the manometer readings and room temperature records for what it would be at 0°.

(3) The percentage of the carbon dioxide reduced.

(4) The value of k given by the expression $1/t \log C_o/C_t$ ($t =$ 1 minute).

Series I.—Time of Circulation = 40 *minutes.*

(*a*) Temperature = 750°.

t.	P_{CO_2}.	CO_2 reduced, per cent.	k (t = 1 minute).
0	313·7	—	—
2820	309·6	1·3	0·00000198
4830	307·2	2·1	0·00000207
5280	306·7	2·2	0·00000184
6960	306·0	2·4	0·00000155
		Mean	0·00000186

(*b*) Temperature = 800°.

0	301·7	—	—
840	297·7	1·3	0·00000685
3720	284·5	5·7	0·00000685
4260	281·2	6·8	0·00000717
5160	277·2	8·1	0·00000717
8040	268·2	11·1	0·00000633
		Mean	0·00000687

(*c*) Temperature = 900°.

0	315·6	—	—
60	303·0	4·0	0·000295
120	288·9	8·4	0·000319
180	273·4	13·4	0·000346
240	260·5	17·5	0·000347
300	250·9	20·5	0·000332
360	241·5	23·5	0·000323
480	226·5	28·2	0·000300
660	205·2	35·0	0·000285
		Mean	0·000318

Series I.—Time of Circulation = 40 *minutes* (continued).

(*d*) Temperature = 1000°.

t.	P_{CO_2}.	CO_2 reduced, per cent.	*k* (*t* = 1 minute).
0	284·4	—	—
15	253·8	10·7	0·00330
30	223·9	21·3	0·00346
45	193·5	32·0	0·00371
60	171·1	47·4	0·00368
75	149·6	53·7	0·00372
90	131·6	64·5	0·00372
120	100·9	74·3	0·00375
150	73·1	83·3	0·00393
		Mean	0·00368

(*e*) Temperature = 1100°.

0	297·8	—	—
5	274·1	7·9	0·00720
10	248·9	16·4	0·00779
15	222·6	25·3	0·00843
20	196·4	34·0	0·00904
25	169·4	43·2	0·00981
30	147·1	50·6	0·01021
35	130·3	56·3	0·01026
		Mean	0·00896

Series II.—Time of Circulation = 12 *minutes.*

(*a*) Temperature = 800°.

t.	P_{CO_2}.	CO_2 reduced, per cent.	*k* (*t* = 1 minute).
0	242·1	—	—
1380	224·2	7·4	0·0000242
2820	212·7	12·1	0·0000200
4260	204·0	15·7	0·0000175
5700	197·6	18·4	0·0000155
		Mean	0·0000193

(*b*) Temperature = 900°.

0	242·3	—	—
5	238·6	1·5	0·00134
10	235·0	3·0	0·00134
15	231·6	4·4	0·00128
30	221·7	8·5	0·00128
45	212·2	12·4	0·00120
120	174·1	28·1	0·00115
180	150·3	38·0	0·00104
240	135·8	44·0	0·00097
300	124·1	48·8	0·00096
		Mean	0·00117

Series II.—Time of Circulation=12 *minutes* (continued).

(*c*) Temperature=1000°.

t.	p_{CO_2}.	CO_2 reduced, per cent.	*k* (*t*=1 minute).
0	201·0	—	—
5	177·6	11·6	0·01074
13	144·7	28·0	0·01097
18	128·9	35·9	0·01060
23	114·6	43·0	0·01061
28	101·0	49·7	0·01066
33	88·7	55·9	0·01077
38	77·9	61·2	0·01083
43	68·2	66·1	0·01092
48	57·7	71·3	0·01130
53	48·4	75·9	0·01166
58	41·0	79·6	0·01190
		Mean	0·01099

(*d*) Temperature=1050°.

0	193·7	—	—
1	183·2	5·4	0·02420
2	173·5	10·4	0·02400
3	164·0	15·3	0·02413
4	155·2	19·9	0·02407
5	146·5	24·4	0·02426
10	109·7	43·4	0·02469
15	81·7	57·8	0·02500
20	60·7	68·7	0·02520
		Mean	0·02444

(*e*) Temperature=1100°.

0	188·7	—	—
1	176·9	6·2	0·02810
2	165·5	12·3	0·02850
3	153·6	18·6	0·02980
4	141·7	24·9	0·03112
5	130·0	31·1	0·03238
10	82·0	56·6	0·03620
		Mean	0·03101

On comparing these two series it is apparent that the relative values for the rates of reaction at different temperatures are not very far wrong; for they are not greatly affected by the alteration of the most important experimental condition—the time of circulation. The percentage reduction at each temperature is, in fact, practically proportional to the time of circulation, as much change taking place at the end of forty minutes in the "40-minute" series as at the end of twelve minutes in the "12-minute" series. It will be noticed, however, that in both series the value of *k* at a temperature of 1100° increases throughout the experiment. That is to say, as the concentration of the carbon dioxide decreases, the fraction reduced during a given interval of time increases. From this we concluded that, even with a rapid rate of circulation of the gases, the contents of the reaction-tube were not changed sufficiently rapidly at 1100° to ensure that excess of carbon dioxide was always present.

A series of experiments was therefore made at the higher temperatures, using a mixture of carbon dioxide and nitrogen containing 20 per cent. of carbon dioxide, and the time of circulation was made shorter by the introduction of an additional "fall-tube" to the Sprengel pump. The results were as follow:

Series III.—Carbon Dioxide and Nitrogen (CO_2 = 20 *per cent.*).

(*a*) Temperature = 900°. Time of circulation = 6·5 minutes.

t.	p_{CO_2}.	CO_2 reduced, per cent.	*k* (*t* = 1 minute).
0	80·4	—	—
60	75·3	6·3	0·000475
120	70·2	12·7	0·000491
180	66·0	17·9	0·000477
240	62·8	21·9	0·000443
300	59·9	25·5	0·000426
		Mean	0·000463

(*b*) Temperature = 950°. Time of circulation = 6·5 minutes.

0	72·6	—	—
5	70·6	2·7	0·00242
10	68·6	5·5	0·00246
15	66·7	8·1	0·00245
25	62·1	14·4	0·00271
35	57·6	20·6	0·00287
55	50·2	30·8	0·00291
85	40·9	43·6	0·00293
115	34·4	52·6	0·00282
175	22·7	68·7	0·00285
235	11·1	84·7	0·00347
295	5·8	92·0	0·00372
		Mean	0·00287

(*c*) Temperature = 1000°. Time of circulation = 7 minutes.

0	78·3	—	—
1	76·3	2·5	0·0112
2	74·4	5·0	0·0113
3	72·6	7·3	0·0111
8	63·5	18·9	0·0113
13	54·1	30·9	0·0124
18	45·5	41·9	0·0131
23	38·0	51·5	0·0136
28	31·3	60·0	0·0142
33	25·2	67·8	0·0150
		Mean	0·0125

Series III.—Carbon Dioxide and Nitrogen ($CO_2=20$ *per cent.*) (continued).

(*d*) Temperature = 1050°. Time of circulation = 6 minutes.

t.	p_{CO_2}.	CO_2 reduced, per cent.	*k* (*t* = 1 minute)
0	54·2	—	—
1	48·9	9·8	0·0447
2	44·1	18·6	0·0448
3	39·4	27·3	0·0459
4	35·1	35·3	0·0472
5	31·4	42·1	0·0474
6	28·1	48·1	0·0475
7	25·2	53·5	0·0475
8	22·4	58·7	0·0479
9	20·0	63·1	0·0481
10	17·7	67·3	0·0486
11	15·8	70·8	0·0486
12	14·4	73·4	0·0480
13	12·9	76·2	0·0479
		Mean	0·0473

(*e*) Temperature = 1100°. Time of circulation = 4·5 minutes.

0	46·5	—	—
1	36·2	22·2	0·1088
2	27·5	40·9	0·1141
3	20·9	55·0	0·1158
4	15·8	66·0	0·1172
5	11·3	75·7	0·1229
6	8·7	81·3	0·1213
7	6·8	85·4	0·1191
8	5·0	89·2	0·1210
		Mean	0·1175

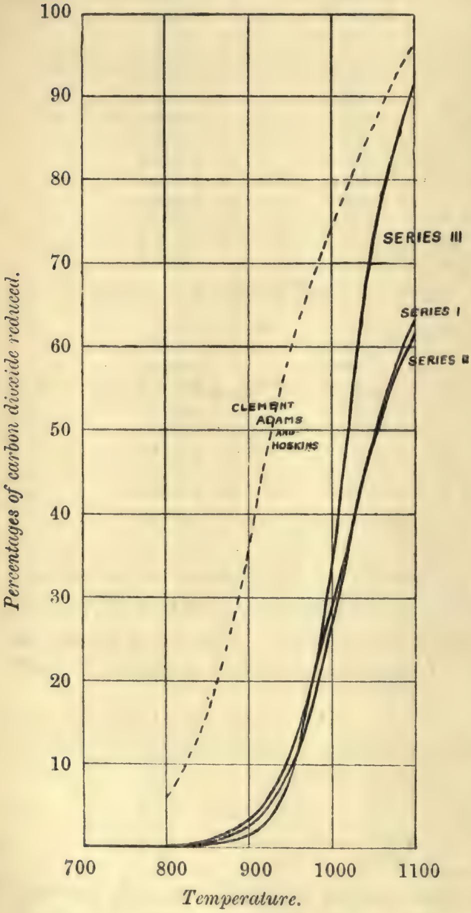
In order to make the experiments in this third series strictly comparable amongst themselves, it is necessary to make a correction for the differences in the times of circulation. The mean values of *k* thus corrected, for a time of circulation of five minutes in each case, are:

Temperature.	*k* (*t* = 1 minute).	Carbon dioxide reduced after 10 minutes, per cent.
900°	0·00060	1·4
950	0·00374	8·3
1000	0·01764	33·3
1050	0·05760	73·4
1100	0·10570	91·3

From the values of *k* the percentages of carbon dioxide reduced at the end of a given time can be calculated; in the third column are given the percentages reduced after ten minutes' circulation.

The curve obtained by plotting these percentages as ordinates with temperatures as abscissæ should be of a similar type to those derived from Clement, Adams, and Hoskins' experiments with different "times of contact" between the carbon dioxide and the carbon (p. 832); for, although no absolute value can be assigned to the time of contact in our experiments (for the percentages given in the above table it would probably be under one second), the percentage of the carbon dioxide reduced after a given interval of time of circulation can be regarded as having taken place with the *same* time of contact in each experiment of the series. In Fig. 2 are given a curve for a time of contact of five seconds obtained from Clement, Adams, and Hoskins' experiments, shown in dotted line; and our curves for a time of contact of x seconds ($x<1$), obtained from the three series of experiments described in this paper. Of the three last, that obtained from the experiments in Series III (20 per cent. carbon dioxide) shows clearly that we were correct in believing that when pure carbon dioxide was used, the amount of change that took place at the higher temperatures under the conditions of the experiments did not truly represent the maximum rate of reduction at those temperatures relative to the lower temperatures, for the reason that the fastest rate of circulation of the gases employed did not remove the products of reduction rapidly enough from the carbon surface. The admixture of nitrogen with the carbon dioxide causes a general retardation of the rate of reduction throughout the series at different temperatures, and enables the true relative rates at the higher temperatures to be appreciated. If a sufficiently rapid passage of the pure carbon

FIG. 2.



dioxide could have been effected, the percentages reduced at 1000° and 1100° would undoubtedly have fallen on a curve lying above that given by the "20 per cent." series.

The results of this "20 per cent." series are of technical value in that they represent what is generally considered to take place in producer-gas manufacture. The usual statement is that in an air-blown gas-producer "directly above the grate carbon dioxide is formed, but this is converted into carbon monoxide on passing through the column of heated fuel above it" ("An introduction to the study of metallurgy," Roberts-Austen, p. 231). Whether the carbon dioxide arises from the direct union of the carbon and oxygen, or from the subsequent oxidation of carbon monoxide first formed, there is no doubt but that near the point of introduction of the air-blast it is the main oxidation product found (Karl Wendt, *Stahl und Eisen*, 1906, **26**, 1186). The complete combustion of the oxygen in the air would give a mixture containing about 20 per cent. of carbon dioxide and 80 per cent. of nitrogen, such as was used in the experiments of Series III. The curve in Fig. 2 shows, therefore, that for the short time of contact that can be allowed in the manufacture of producer-gas, a temperature of over 1100° must prevail in the fuel-bed if the fairly complete reduction of carbon dioxide desired is to be obtained.

Our curves show, in all the series of experiments that we have made, a rapid falling off in the amount of reduction during a given time when the temperature falls below 1000°. In this respect they differ in degree from the curve obtained from Clement, Adams, and Hoskins' figures, and it appears to us probable that, as in our experiments with pure carbon dioxide at 1000° and 1100°, a much more rapid stream of gas should have been passed in order to show the true difference between the rates of reduction in their experiments at 1000°, 900°, and 800°. We should have expected, however, that their most rapid streams at 800° and 900° (giving times of contact of 1·55 and 2·17 seconds respectively) would have sufficed to show the true difference between the rates of reduction at those two temperatures, for the difference is very marked and the rates are both fairly slow.

ALTOFTS.

LXXXIX.—*The Combustion of Carbon.*

By Thomas Fred Eric Rhead and Richard Vernon Wheeler.

The question as to what is the first reaction that takes place when carbon burns in oxygen has long been a subject of controversy.

The commonly accepted view is that the first product is carbon dioxide, which, in contact with an excess of incandescent carbon, is immediately reduced to carbon monoxide, thus *:

$$(a)\ C + O_2 = CO_2.$$
$$(b)\ CO_2 + C = 2CO.$$

On the other hand, the classical investigations of Dixon on the rates of explosion of mixtures of gaseous carbon compounds with oxygen, and of H. B. Baker on combustion in dried oxygen, support the belief that carbon burns directly to carbon monoxide:

$$(c)\ 2C + O_2 = 2CO,$$

and that any carbon dioxide found in the products is only formed by the secondary combustion of the monoxide:

$$(d)\ 2CO + O_2 = 2CO_2.$$

Dixon's work leaves no room for doubt but that in the burning of *gaseous* carbon, carbon monoxide is produced before carbon dioxide; for example, in the explosion of cyanogen (Dixon, Strange, and Graham, Trans., 1896, **59**, 759) it is shown that the velocity of the explosion-wave is higher when the gas is half-burnt to carbon monoxide than when there is enough oxygen present to burn it completely. Moreover, the substitution of inert nitrogen for the additional molecular volume of oxygen required for complete combustion produces less retardation. So far as the propagation of the explosion-wave is concerned, therefore, the second molecule of oxygen is inert. This is well shown by the following rates of explosion:

Mixture of gases	$C_2N_2 + O_2$.	$C_2N_2 + 2O_2$.	$C_2N_2 + O_2 + N_2$.
Rate of explosion (metres per second) ...	2728	2321	2398

Further, the flame is not only propagated more quickly, but the pressure is higher and the reaction sooner completed in the first than in the second case. The only conclusion to be drawn from these results is that the formation of carbon monoxide precedes that of carbon dioxide.

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* This view seems to have been controverted by Tunner so long ago as 1861, and in 1872, Sir Lowthian Bell, in his "Chemical Phenomena of Iron Smelting" (Section II, pp. 4—9), argued strongly in favour of the view that carbon monoxide and not carbon dioxide is the initial product of the combustion of carbon.

H. B. Baker's experiments (*Phil. Trans.*, 1888, **179**, *A*, 571) certainly point to the conclusion that when solid carbon burns in oxygen its combustion is effected in two stages; that it forms first carbon monoxide, which, if circumstances are favourable, undergoes further oxidation to carbon dioxide.

C. J. Baker (Trans., 1887, **51**, 249) undertook experiments with the object of ascertaining the nature of the gases produced on heating carbon that had absorbed oxygen at low temperatures. He found, as had been stated by Angus Smith (*Proc. Roy. Soc.*, 1863, **12**, 424), that moist oxygen which had been absorbed by carbon at −12° was given up as carbon dioxide when the carbon was heated to 100°. On the other hand, C. J. Baker found that dried carbon which had absorbed dried oxygen (dried by phosphoric oxide) at +12° yielded only traces of gas on heating until a temperature of 450° was reached. The gases then obtained consisted mainly of carbon monoxide. Hs drew the conclusion that carbon is burned directly to carbon monoxide by the absorbed oxygen.

The experimental evidence in support of the view that carbon dioxide is the first product of the burning of solid carbon is derived chiefly from some work by J. Lang (*Zeitsch. physikal. Chem.*, 1888, **2**, 168), which can be summarised as follows:

(1) Oxygen was passed over gas-carbon contained in a glass tube heated to 500°, at which temperature it was found that the gas-carbon could not reduce carbon dioxide. The products of combustion varied with the speed of passage of the oxygen, the carbon monoxide formed being less the slower the gas-stream, and disappearing altogether with very slow streams.

The conclusion drawn by Lang from these experiments was that the carbon monoxide found with quick streams was produced by the reduction of the carbon dioxide first formed, owing to local heating of the carbon. With very slow streams no local heating would occur, and therefore there was no reduction of carbon dioxide.

(2) A mixture of oxygen and carbon monoxide was passed at different speeds over carbon heated at 500°. With slow gas streams the whole of the oxygen was converted into carbon dioxide, and the carbon monoxide passed through the tube unchanged. With rapid streams more carbon monoxide was found in the products than was present in the original mixture, some of the carbon dioxide first formed being reduced by the carbon.

Lang therefore concluded that, since the oxygen was converted into carbon dioxide under such conditions that the carbon monoxide present was not acted on, the carbon dioxide must have been formed without the intermediate formation of carbon monoxide.

Dixon, in a paper entitled "The mode of burning of carbon" (Trans., 1899, **75**, 630), criticised Lang's conclusions. He pointed out that the first series of experiments merely showed that carbon dioxide was the *final* product when oxygen was passed slowly over coke heated at 500°, and that there was no direct contradiction of the supposition that carbon monoxide was the first product of oxidation of the coke, the carbon monoxide molecules thus formed being further oxidised to carbon dioxide. Lang's second series of experiments, which appeared to dispose of this possibility, Dixon was unable to confirm; and he gave results of experiments which were at variance with those of Lang.

Since this paper of Dixon's, there does not appear to have been any further attempt to produce experimental evidence in favour of the view that carbon burns first to form carbon dioxide; but it cannot be said that the alternative, which the work of Dixon and Baker supports, has received universal acceptance. Haber, for example ("Thermodynamics of Technical Gas Reactions," Eng. Ed., p. 255), considers the primary reaction to be:

$$C + O_2 \rightleftharpoons CO_2,$$

the adjustment of the equilibrium being brought about by the secondary reaction:

$$CO_2 + C \rightleftharpoons 2CO.$$

This adjustment would or would not take place according as the carbon dioxide had time to react or not.

Whilst it appeared to be impossible to obtain *direct* evidence as to the first product of oxidation of solid carbon, we hoped that, indirectly, a study of the relative rates at which the various reactions between oxygen, carbon, carbon monoxide, and carbon dioxide proceeded under the same experimental conditions, might enable us to form some opinion as to which were the more likely to take precedence at different temperatures.

If it could be shown that either reaction (*a*) or reaction (*c*) (p. 846) proceeded at a temperature at which, under the same experimental conditions, the rates of reactions (*b*) and (*d*) were inappreciable, the problem would be solved.

It may be said at once that we have been unable to arrive at a complete solution of the problem in such a simple manner; for at no temperature at which the rate of oxidation of carbon is appreciable could we obtain conclusive evidence of the primary formation, *to the exclusion of the other*, of either carbon monoxide or carbon dioxide.

Our experiments show (1) that some carbon monoxide is produced during the oxidation of carbon at low temperatures, under conditions which do not admit of the reduction of carbon dioxide by carbon. On the other hand, (2), carbon dioxide is undoubtedly produced at low temperatures in quantity which cannot be altogether accounted for by the supposition that carbon monoxide is first formed and then oxidised to carbon dioxide.

When carbon is burned at low temperatures, therefore, carbon dioxide and carbon monoxide are produced *simultaneously.*

The question naturally arises as to what reaction between oxygen and carbon can account for this simultaneous production of the two oxides. The conclusions to which we have come regarding this problem, together with a description of the experiments on which these conclusions are founded, form the subject of a separate paper.

EXPERIMENTAL.

P. Farup (*Zeitsch. anorg. Chem.*, 1906, **50**, 276) has determined the rate of reaction between oxygen and graphite (arc-lamp carbon) at temperatures of 455°, 485°, and 515°; and between air and graphite at 485° and 515°. The air or oxygen was passed in a continuous stream through a heated bulb-tube of porcelain containing the graphite in the form of a rod. Experiments, in the same apparatus, were also made by Farup on the rate of reduction of carbon dioxide by graphite. He found that the rate or reduction of carbon dioxide at 850° was about the same as the rate of oxidation of graphite at 450°; and that the temperature-coefficient k_{t+10}/k_t of the latter reaction over the range 450—500° was about 1·50.

Our determinations were made with highly purified wood charcoal under the same experimental conditions, and in the same apparatus as those of the rate of reduction of carbon dioxide already described (this vol., p. 835).

A given volume of air or oxygen was circulated continuously through the carbon contained in a porcelain tube, and heated in an electric resistance furnace. The weight of carbon used in each experiment was about 2·5 grams, and it was sieved through a 10- and on a 30-mesh sieve so as to be of uniform size. It occupied the middle 9 cm. of the length of the porcelain tube, which was of 1·2 cm. bore.

A series of three by-passed sampling-tubes, and a by-passed absorption-tube, were included in the circuit of the gases (see diagram on p. 844), and could be used or omitted as required for different experiments. The absorption-tube, *R*, for the removal of carbon dioxide as soon as formed, was placed between the reaction tube and a calcium chloride drying-tube. It consisted of a cylindrical vessel, 27 cm. long and 4 cm. in diameter. Soda-lime mixed with small pieces of potassium hydroxide filled this vessel to within 5 or 6 cm. from each of the ends, which contained pure stick potassium hydroxide broken into pieces about 4 mm. cube. This admixture of potassium hydroxide with the soda-lime prevented moisture, given off from the latter when carbon dioxide is absorbed, from being carried away by the gases, which were further dried by the calcium chloride.

We will first give the details of a series of three determinations of the rate of oxidation of carbon by air at 350°, 400°, and 500° respectively. In the experiments at 350° and 400° the sampling-tubes were shut off from, and the absorption-tube turned on to, the circuit, and the rate of oxidation determined from readings of the pressure inside the apparatus at given intervals of time. In the experiment at 500°, in which there was a considerable formation of carbon monoxide, both sampling-tubes and absorption-tube were employed, and the rate of disappearance of oxygen determined from the partial pressures at given intervals of time. These partial pressures were calculated from the total pressures in the apparatus, and the analyses of the samples of gases shut off periodically during the course of the experiment.

We have already commented on the fact that, in determining the relative rates of gaseous reactions taking place on or with a surface, it is essential that the surface should be in the same condition before each experiment is begun. In our experiments on the rate of reduction of carbon dioxide by carbon, this was effected by heating the carbon (in the reaction-tube) to 1100°, and exhausting at that temperature. In the present experiments on the oxidation of carbon, treatment of the carbon in this manner destroyed their relative value, for a reason that will appear later.

Starting with a carbon surface that had been exhausted at 1100°, it was found necessary, in order to obtain comparable values for the rate of reaction at different temperatures, to make a series of consecutive determinations at the experimental temperature, keeping that temperature rigidly constant between each determination. The first three or four determinations showed a rapidly decreasing rate of reaction, but after a time a value was obtained which did not vary from one experiment to another.

This constant rate was regarded as the "normal" rate of reaction at the particular temperature employed; thus, the experiments detailed below are the final ones of series made at each temperature with successive charges of air until a constant rate of reaction was obtained.

In the tables that follow:

t = the time in minutes from the beginning of each experiment.

P=the total pressure in the apparatus, determined from manometer readings, and corrected for a temperature of 0°.

P_{O_2},P_{CO}=the partial pressures of oxygen and carbon monoxide.

k_{O_2}=the rate of disappearance of oxygen, calculated from the partial pressures (concentrations) by means of the expression $1/t \log C_o/C_t$ (t=1 minute).

Experiments with Air.

T=350°.

t.	P (mm.).	P_{O_2} (mm.)	k_{O_2}.
0	406·4	78·4	—
360	402·7	74·7	0·0000583
720	399·7	71·7	0·0000533
1440	394·0	66·0	0·0000517
2880	383·1	55·1	0·0000517
3240	378·7	50·7	0·0000583

The final gas contained 0·20 per cent. of carbon monoxide, corresponding with a partial pressure of 0·75 mm.

T=400°.

t.	P (mm.).	P_{O_2} (mm.).	k_{O_2}.
0	417·8	87·7	—
120	405·2	75·1	0·000562
240	395·0	64·9	0·000545
360	385·6	65·5	0·000550
480	376·0	46·5	0·000574
600	370·0	39·9	0·000570
720	364·0	33·9	0·000573

The final gas contained 0·60 per cent. of carbon monoxide, equivalent to a partial pressure of 2·2 mm.

T=500°.

		Gas analysis, per cent.				
t.	P (mm.).	CO.	O_2.	P_{CO} (mm.).	P_{O_2} (mm.).	k_{O_2}.
0	465·2	nil	20·7	—	96·4	—
30	435·0	8·6	4·3	37·4	18·7	0·0237
45	424·3	9·1	2·1	38·6	8·9	0·0230
60	418·3	9·8	0·8	41·0	3·3	0·0244
120	408·4	9·0	nil	36·7	—	—

It is to be noted, in the first place, that the temperature-coefficient k_{t+10}/k_t, calculated from the mean values of k at the three temperatures recorded, is 1·52; that is to say, practically identical with that found by Farup for the oxidation of graphite over about the same range of temperature.

Comparison with the relative rates of reduction of carbon dioxide at different temperatures, shows that under the same conditions of experiment the rate of oxidation of carbon at 500° is about equal to the rate of reduction of carbon dioxide at 1130°.

The most important result is, however, the formation of so much carbon monoxide during the oxidation of carbon at 500°. Whilst at 350° and 400° traces of carbon monoxide were found in the gases at the end of fifty-four and twelve hours' circulation respectively, at 500° the gases at the end of thirty minutes contained as much as 8·6 per cent.

Supposing that the first reaction between oxygen and carbon produces carbon dioxide, and that any carbon monoxide found in the final products arises from the reduction of some of this carbon dioxide by excess of carbon, two assumptions can be made as to the means by which the reduction is effected.

It can be assumed that the air in the experiment at 500° was transformed, after it had passed through the first few centimetres of the column of carbon, into a mixture containing about 20 per cent. of carbon dioxide and 80 per cent. of nitrogen, no carbon monoxide having yet been formed. Partial reduction of the carbon dioxide then took place during the passage of this mixture through the remainder of the carbon heated at 500°.

This cannot be the case, however, for we have shown that the rate of reduction of carbon dioxide under like experimental conditions is hardly appreciable even at 850°.

The second assumption, that used by Lang (*supra cit.*) of local heating up of the carbon due to its rapid oxidation, is more difficult to dispose of.

Calculation from the partial pressures in the experiment at 500° shows that at the end of thirty minutes an amount of carbon monoxide equivalent to 37·4 mm. had been produced, and that at the same time carbon dioxide equivalent to 48·9 mm. had been formed and absorbed by the soda-lime and potassium hydroxide. That is to say, if it is assumed that carbon dioxide was the sole first product of oxidation of the carbon, about 28 per cent. of it had been reduced.

For this amount of reduction to take place in thirty minutes, we calculate (from the ascertained rates of reduction of carbon dioxide under the same conditions of experiment) that the carbon would have to be raised locally to a temperature of over 1175°.

Before discussing the matter further, we will give one of the results of a series of experiments made with pure oxygen. The experiment chosen is one of several made at a temperature of 500°, at which temperature a considerable quantity of carbon monoxide is formed. The time of circulation of the gases was the same as in the experiments with air, and the carbon dioxide formed was removed in the same manner. The result was as follows: *

Experiment with Oxygen.

$T = 500°$.

t.	P (mm.).	P_{O_2} (mm.).	P_{CO} (mm.).	k_{O_2}.
0	372·8	372·8	—	—
30	160·4	73·0	87·4	0·0236

The gases at the end of the experiment contained 54·5 per cent. of carbon monoxide.

The rate of disappearance of oxygen is no greater in this experiment with pure oxygen than in the comparative experiment with air at 500°. This result agrees with numerous other comparative experiments that we have made with oxygen and with air at temperatures below 500°.

If at these comparatively low temperatures there were any pronounced local heating, one would expect to find that the mixture of an inert gas with the oxygen would, by minimising the amount of local heating, decrease the rate of oxidation. Any decrease in the rate, due to such cause, should, moreover, be very marked; for we have shown that an increase in the temperature of the carbon of 50° between 350° and 500° increases the rate of reaction five- or six-fold.

The fact that the rate of oxidation when either air or pure oxygen is used is the same, the rate of disappearance of oxygen being directly proportional to its partial pressure (concentration) in both cases, brings us to the conclusion that no local heating of the carbon can account for the formation, by reduction of carbon dioxide, of so much carbon monoxide as is shown in these experiments at 500°. That when the oxygen first enters the column of carbon some rise in temperature must take place owing to the heat of the reaction, is incontrovertible; but it would appear that a rapid dissipation of this heat takes place throughout the mass of the carbon, and through the walls of the containing vessel, and that such carbon molecules as may be raised to a temperature sufficiently high to reduce carbon dioxide are few in number.

The question now arises whether, if oxidation of the carbon monoxide could be prevented, any carbon dioxide would be found in the products of combustion of carbon. That is to say, granted that the carbon monoxide found in the products of combustion does not arise from the reduction of carbon dioxide, does the carbon dioxide found arise solely from the oxidation of carbon monoxide?

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* No samples were taken during the course of this experiment, for the rapid rate of disappearance of oxygen prevented such samples from being in any way representative of the total contents of the apparatus, and therefore rendered them useless for the purpose of calculating the partial pressures of oxygen and carbon monoxide at different intervals of time.

We have attempted to answer this question by experimenting with mixtures of carbon monoxide and oxygen, and determining their rates of combination when circulated over carbon heated at different temperatures. The experiments were made in the same apparatus and under the same conditions as those already described.

In the three experiments described below a mixture of carbon monoxide and oxygen in combining proportions ($2CO + O_2$) was circulated through carbon heated at 250°, 300°, and 400° respectively. The time of circulation of the gases was, as before, thirty-five minutes. The carbon dioxide formed was removed by the absorption tube.

Experiments with Carbon Monoxide and Oxygen.

$T = 250°$.

	P_{CO} (mm.).	P_{O_2} (mm.).
Original	265·5	125·4
Final, after 288 hours	251·6	105·2
Difference...........	13·9	20·2

The 13·9 mm. of carbon monoxide that have disappeared required 6·9 mm. of oxygen to form carbon dioxide. This leaves 13·3 mm. of oxygen that have combined with the carbon forming, ultimately, carbon dioxide. The ratio between these two quantities is 1·93.

Similarly, for the experiments at 300° and 400° the ratios were:

$T = 300°$.

$$\text{Ratio}: \frac{\text{Oxygen combined with carbon}}{\text{Oxygen combined with carbon monoxide}} = 1·55.$$

$T = 350°$.

$$\text{Ratio}: \frac{\text{Oxygen combined with carbon}}{\text{Oxygen combined with carbon monoxide}} = 0·84.$$

Let us consider first the experiment at 250°. Pure oxygen circulated through carbon heated at 250° produces mainly carbon dioxide, as the following experiment (made under the same conditions as all the others) shows:

Experiment with Oxygen.

$T = 250°$.

t.	P (mm.).	P_{CO} (mm.).	k_{O_2}
0	390·5	—	—
1440	386·8	—	0·0000028
2880	383·9	—	0·0000025
4320	381·0	—	0·0000025
5760	375·6	—	0·0000030
8700	366·6	2·0	0·0000029

The gases at the end of this experiment were found to contain 0·60 per cent. of carbon monoxide, equivalent to a partial pressure of 2·0 mm. This was formed whilst 23·9 mm. of oxygen were burnt. That is to say, about 4 per cent. only of the oxygen burnt appeared in the products of combustion as carbon monoxide.

If it is assumed that the first reaction between carbon and oxygen produces carbon monoxide, and that any carbon dioxide found is due to the subsequent oxidation of this carbon monoxide by excess of oxygen, it would appear that the rate at which carbon monoxide combines with oxygen over the carbon surface at 250° must be much faster than its rate of formation from carbon.

To return to the experiment with carbon monoxide and oxygen over carbon at 250°. The result shows that the rate of combination of the oxygen with the carbon was 0·00000281.* This is about the same rate as was found when pure oxygen was used.

On the other hand, the rate of disappearance of oxygen in combination with carbon monoxide was 0·00000142; that is to say, about *half as fast* as the rate of combination of oxygen with carbon.

This fact would appear at once to discount the hypothesis that carbon monoxide is formed first when oxygen combines with carbon; but, as Dixon in his criticism of Lang's work points out, the *nascent* carbon monoxide molecules may combine with oxygen rapidly on or near the surface of the carbon, whilst the carbon monoxide originally present is comparatively inert.

Let us now compare the results of the three experiments with a mixture of carbon monoxide and oxygen. The ratio between the rate of combination of oxygen with carbon and the rate of combination of oxygen with carbon monoxide is 1·9 at 250°. At 300° it is 1·5, and at 400° it is 0·8. Now if carbon monoxide is the sole first product of combustion of carbon, this decrease in the ratio with increasing temperature must mean either (1) that the rate of combustion of carbon monoxide increases more rapidly between

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* Calculated from the expression $1/t \log C_0/C_t$, the fall in concentration of the oxygen due to combination with carbon being 13·3 mm. at the end of 288 hours.

250° and 400° than does the rate of combustion of carbon; or (2) that the higher the temperature (within the limits 250° to 400°) the greater is the number of nascent carbon monoxide molecules that escape oxidation at the surface.

Neither of these explanations is satisfactory. The first demands that the lower the temperature of oxidation of carbon the greater the quantity of carbon monoxide in the products, whereas the reverse is the case. The second implies that the more rapidly the nascent carbon monoxide molecules are carried away from the surface the greater is the number that remain unoxidised. If this were so, a rapid stream of air or oxygen passed through carbon heated at, say, 400°, should yield more carbon monoxide in proportion to carbon dioxide than a slow stream. We have found the reverse to be the case.

We arrive, therefore, at the conclusion given in the theoretical portion of this paper, that when carbon burns at low temperatures there is a simultaneous production of the two oxides.

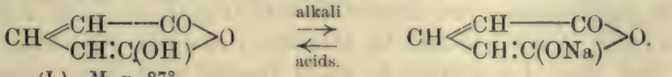
ALTOFTS.

XC.—*The Chemistry of the Glutaconic Acids. Part III. Glutaconic Acid and its β-Alkyl Derivatives.*

By NORMAN BLAND and JOCELYN FIELD THORPE.

THE acids described in this communication are those which were included in class III (Trans., 1911, **99**, 2209), and are characterised by having both hydrogen atoms of the methylene group unsubstituted. The acids contained in this class are therefore glutaconic acid and its β-monosubstituted derivatives. Unfortunately, it is a matter of some considerable difficulty to prepare the β-alkyl derivatives of glutaconic acid, and the only acids of this kind which we have as yet been able to obtain are β-methylglutaconic acid and β-phenylglutaconic acid. An examination of the properties of these acids showed at once that the attachment of an alkyl group to the β-carbon atom has a most marked effect on the condition of the molecule, and that a complete study of the behaviour of an homologous series of these acids, and more especially of their esters, is likely to throw light on the problem of the structure of glutaconic acid. Experiments are therefore in progress, having for their object the discovery of a general method by which the β-alkyl derivatives can be prepared, but in the meantime it has been thought advisable to record the results of our experiments with the already known acids in order that their properties may be correctly recorded in the literature.

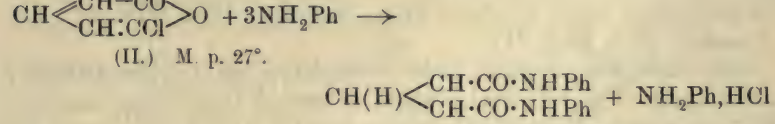
Glutaconic Acid, $CO_2H\cdot CH\cdot CH(H)\cdot CH\cdot CO_2H$.—In spite of several attempts (compare Perkin and Tattersall, Trans., 1905, **87**, 361; Feist, *Annalen*, 1909, **370**, 54) it has not been found possible to obtain this acid in more than one modification. The anhydride of glutaconic acid was first prepared by Buchner (*Ber.*, 1890, **23**, 706; compare also *Ber.*, 1894, **27**, 881) by the action of acetyl chloride, and was subsequently investigated by Perkin and Tattersall (*loc. cit.*). It is described as a crystalline solid melting at 87°, and dissolving in aqueous sodium carbonate with immediate conversion into the sodium salt of the original acid. Our experiments on the formation of this anhydride show that pure acetyl chloride is quite without action on glutaconic acid under the conditions described by Buchner, and that it is only when acetyl chloride containing phosphorus trichloride (Kahlbaum's acetyl chloride II) is used that anhydride formation occurs. The product is not the normal anhydride, but is 6-hydroxy-α-pyrone (I). This is shown by the fact that it gives an intense green coloration with ferric chloride, and behaves on titration with alkali as a monobasic acid:



$$\mathrm{CH}\left\langle\begin{matrix}\mathrm{CH}\text{——}\mathrm{CO}\\ \mathrm{CH{:}C(OH)}\end{matrix}\right\rangle\mathrm{O} \quad \underset{\text{acids.}}{\overset{\text{alkali}}{\rightleftarrows}} \quad \mathrm{CH}\left\langle\begin{matrix}\mathrm{CH}\text{——}\mathrm{CO}\\ \mathrm{CH{:}C(ONa)}\end{matrix}\right\rangle\mathrm{O}.$$

(I.) M. p. 87°.

No trace of the normal anhydride could be detected, although the chloroanhydride (6-chloro-α-pyrone) (II) is always produced in small amount. The constitution of this substance is proved by the formation of the dianilide of glutaconic acid (III) with aniline (see also Trans., 1911, **99**, 2225):

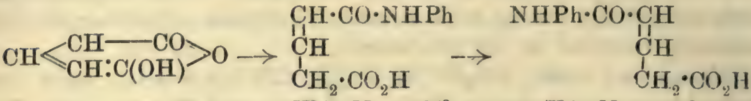


$$\mathrm{CH}\left\langle\begin{matrix}\mathrm{CH{-}CO}\\ \mathrm{CH{:}CCl}\end{matrix}\right\rangle\mathrm{O} + 3\mathrm{NH_2Ph} \longrightarrow \mathrm{CH(H)}\left\langle\begin{matrix}\mathrm{CH\cdot CO\cdot NHPh}\\ \mathrm{CH\cdot CO\cdot NHPh}\end{matrix}\right. + \mathrm{NH_2Ph,HCl}$$

(II.) M. p. 27°.

(III.) M. p. 228°.

The Aniline Derivatives of Glutaconic Acid.—The only derivative of this type which has been prepared is the semianilide which Perkin and Tattersall (Trans., 1905, **87**, 365) obtained by the action of aniline on the anhydride; the melting point is given as 128—132°. We find that glutaconic acid behaves towards aniline in precisely the same manner as its α-monosubstituted derivatives (compare Trans., 1911, **99**, 2213); thus the hydroxy-anhydride yields the *cis*-semianilide (IV) (m. p. 135°), which is converted at 150° into the *trans*-semianilide (V) (m. p. 167°):



(IV.) M. p. 135°. (V.) M. p. 167°.

It is evident that, as with the α-monosubstituted derivatives, rearrangement to the stable *trans*-modification takes place at a lower temperature than that required to eliminate water to form the hydroxy-anil.

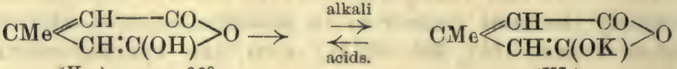
The derivatives of glutaconic acid may be therefore summarised as follows:

	Acid.	Hydroxy-anhydride.	Chloro-anhydride.	*cis*-Semianilide.	*trans*-Semianilide.	Dianilide
Glutaconic acid .... $CO_2H\cdot CH\cdot CH(H)\cdot CH\cdot CO_2H$	138°	87°	27°	135°	167°	228°

The β-Monosubstituted Derivatives of Glutaconic Acid.—The most important feature that distinguishes these acids from all the other members of the series is the ease with which they are converted into their anhydrides by acetyl chloride.

β-Methylglutaconic acid, $CO_2H\cdot CH\cdot CH(H)\cdot CH\cdot CO_2H$, exists in two well-defined forms, one melting at 149°, the other at 115—116°. Both modifications are converted with equal readiness into the anhydride, melting at 90°, by the action of acetyl chloride. From the fact that this anhydride when treated with water gives the modification of higher melting point only, it has been concluded that the acid melting at 149° is the *cis*-modification, and that the modification of lower melting point has the *trans*-configuration. The acid of higher melting point is converted into the acid melting at 115—116° on boiling with alkali, and the reverse change is partly effected by acids. (For a summary of the literature concerning these acids compare Feist, *Annalen*, 1909, **370**, 47; also *Annalen*, 1906, **345**, 81).

Our experiments with these acids have led to the following conclusions: The anhydride, which is formed from either modification by acetyl chloride, is not the normal anhydride, but is the hydroxy-anhydride (6-hydroxy-4-methyl-α-pyrone) (V*a*). It gives an intense purple coloration with ferric chloride, and behaves on titration as a monobasic acid. It is, moreover, readily converted into a crystalline potassium salt (VI), from which the hydroxy-anhydride is regenerated by the action of acids:



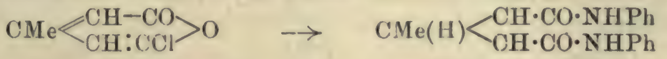
(V*a*.) p. 90° (VI.)

When the hydroxy-anhydride is allowed to remain dissolved in excess of alkali, or if it is converted into the alkali salt of the dibasic acid by excess of alkali in the presence of casein, the acid obtained from the solution on acidifying is the acid of lower melting point (115—116°), and it is therefore evident that this acid is the *cis*-* and not the *trans*-*modification of β-methylglutaconic acid; in fact, these acids, as is shown by the following table, are comparable with the isomeric forms of the α-monosubstituted acids, that is to say, with the only other acids of the "mobile" series which have as yet been isolated in two modifications:

	Trans.	*Cis.*	Hydroxy-anhydride.
β-Methylglutaconic acid	149°	115—116°	90·0°
α-Methylglutaconic ,, ...	145—146°	118°	74·5
α-Ethylglutaconic ,, ...	133—134	108	liquid
α-Benzylglutaconic ,, ...	153—154	139	90·0°

In all these cases the acid formed from the anhydride by the action of water is always the form of higher melting point, and it is only in the presence of excess of alkali or when casein is used that the modification of lower melting point is produced.

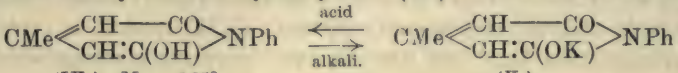
The prolonged action of acetyl chloride leads to the formation of a small amount of the chloro-anhydride (6-chloro-4-methyl-α-pyrone) (VII), the structure of which is shown by the formation of the dianilide (VIII) with aniline:



$$\mathrm{CMe}\Big<\begin{matrix}\mathrm{CH{-}CO}\\ \mathrm{CH{:}CCl}\end{matrix}\Big>\mathrm{O} \longrightarrow \mathrm{CMe(H)}\Big<\begin{matrix}\mathrm{CH\cdot CO\cdot NHPh}\\ \mathrm{CH\cdot CO\cdot NHPh}\end{matrix}$$

(VII.) M. p. 43°. (VIII.) M. p. 209°.

The Aniline Derivatives of β-Methylglutaconic Acid.—Two derivatives of this type have been described, namely, a semianilide melting at 143° which is obtained from the anhydride and aniline, and an anil melting at 162°, prepared by heating the acid with aniline. We find that both forms of β-methylglutaconic acid behave in the same manner towards aniline, and when heated at 150° with the base yield the hydroxy-anil (IX). This substance melts at 165°, and is almost certainly identical with the compound melting at 162°, which has been described as the anil. Its hydroxylic structure is, however, apparent from the fact that it dissolves in alkali carbonates, and can be recovered from the solution on acidifying.



$$\mathrm{CMe}\Big<\begin{matrix}\mathrm{CH{-\!-}CO}\\ \mathrm{CH{:}C(OH)}\end{matrix}\Big>\mathrm{NPh} \underset{\text{alkali.}}{\overset{\text{acid}}{\rightleftarrows}} \mathrm{CMe}\Big<\begin{matrix}\mathrm{CH{-\!-}CO}\\ \mathrm{CH{:}C(OK)}\end{matrix}\Big>\mathrm{NPh}$$

(IX.) M. p. 165°. (X.)

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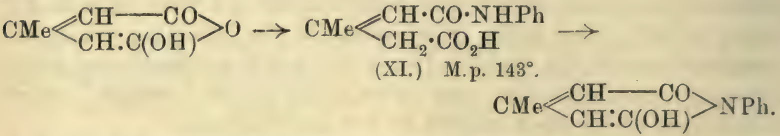
* The terms *cis*- and *trans*- are retained in this paper pending a discussion of the structure of these acids which will appear elsewhere. The term *cis* (labile acid) is given to that modification formed from the hydroxy-anhydride in the presence of casein or alkali. The term *trans* (normal acid) denotes the acid formed by the hydration of the hydroxy-anhydride under ordinary conditions.

Moreover, it behaves on titration as a monobasic acid yielding the alkali salt (X).

The semianilide melting at 143° (XI) is formed from the hydroxy-anhydride and aniline, and, when heated, passes with loss of water into the hydroxy-anil:



$$\mathrm{CMe}\Big<\begin{matrix}\mathrm{CH{-\!\!-}CO}\\ \mathrm{CH{:}C(OH)}\end{matrix}\Big>\mathrm{O} \longrightarrow \mathrm{CMe}\Big<\begin{matrix}\mathrm{CH{\cdot}CO{\cdot}NHPh}\\ \mathrm{CH_2{\cdot}CO_2H}\end{matrix} \longrightarrow \mathrm{CMe}\Big<\begin{matrix}\mathrm{CH{-\!\!-}CO}\\ \mathrm{CH{:}C(OH)}\end{matrix}\Big>\mathrm{NPh.}$$

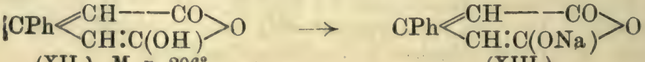
(XI.) M.p. 143°.

β-Methylglutaconic acid, therefore, behaves towards aniline in the same manner as the αγ-disubstituted derivatives, such as αγ-dimethylglutaconic acid, but with this important difference, namely, that the hydroxy-anil is not reconverted into the salt of the semianilide when the neutral solution of its sodium salt is boiled (compare Trans., 1911, **99**, 2219). The stability of the enolic form, which was shown to be conferred on the hydroxy-anil of αβ-dimethylglutaconic acid by the union of the methyl group with the β-carbon atom (Trans., 1911, **99**, 2219), is therefore also exhibited by the acid, which contains a methyl group in the β-position only; in fact, neither the normal form of the anhydride nor the anil of this acid appears to be capable of existence. The derivatives of β-methylglutaconic acid may be therefore summarised as follows:

	trans-Acid.	*cis*-Acid.	Hydroxy-anhydride.	Chloro-anhydride.	Semi-anilide.	Hydroxy-anil.	Di-anilide.
β-Methylglutaconic acid $CO_2H{\cdot}CH{\cdot}CMe(H){\cdot}CH{\cdot}CO_2H$.	149°	115—116°	90°	43°	143°	165°	209°

β-Phenylglutaconic acid, $CO_2H{\cdot}CH{\cdot}CPh(H){\cdot}CH{\cdot}CO_2H$, can be isolated in one modification only (m. p. 154—155°), and with cold acetyl chloride yields an anhydride (m. p. 206°) (Buchner and Schroeder, *loc. cit.*, p. 787; Feist and Pomme, *loc. cit.*, p. 74).

Our experiments with this anhydride show that it is the hydroxy-anhydride (6-hydroxy-4-phenyl-α-pyrone) (XII), and it is certainly remarkable that this fact has not been previously recognised; for example, Buchner and Schroeder (*loc. cit.*, p. 788) state that the stability of this anhydride is such that it crystallises unchanged from its hot solution in alkali carbonates. As a matter of fact, the anhydride certainly dissolves readily in hot aqueous sodium carbonate, and crystals separate on cooling which closely resemble the anhydride in appearance, but are in reality those of the sodium salt of the hydroxy-anhydride (XIII):



$$\mathrm{CPh}\Big<\begin{matrix}\mathrm{CH{-\!\!-}CO}\\ \mathrm{CH{:}C(OH)}\end{matrix}\Big>\mathrm{O} \longrightarrow \mathrm{CPh}\Big<\begin{matrix}\mathrm{CH{-\!\!-}CO}\\ \mathrm{CH{:}C(ONa)}\end{matrix}\Big>\mathrm{O}$$

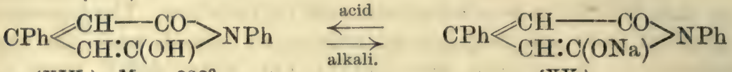
(XII.) M. p. 206°. (XIII.)

The hydroxylic structure of this anhydride is shown, moreover, by the production of a coloration with ferric chloride and by the fact that it behaves as a monobasic acid on titration. The potassium and silver salts are well defined substances, which have the same structure as the sodium salt (XIII), but they differ from the salts of the other hydroxy-anhydrides of this series in being deep yellow.

β-Phenylglutaconic acid possesses considerable interest, because it was on the anhydride of this acid that Feist (Feist and Pomme, *Annalen*, 1909, **370**, 76) first tried his "casein" method for the isolation of the unstable *cis*-forms of the glutaconic acids. From the fact that the silver salt derived from the anhydride and alkali without casein yielded the acid melting at 154—155°, and that in the presence of casein the anhydride was regenerated, he concluded that the cis-form of the acid was, like diethylmaleic acid, unstable, and passed at once into the anhydride when liberated from its salts. Referring to the production of the anhydride in this manner, Feist says (*loc. cit.*, p. 53): "Es ist ausgeschlossen, dass dies Anhydrid *unverändert* die ganze Versuchsserie passirt habe, denn dies Anhydrid ist weder in kaltem Wasser noch in Sodalösung löslich und wäre ausserdem beim Waschen des Silbersalzes mit Alkohol und Aether völlig entfernt worden." It is, of course, quite possible that the anhydride may have passed, as sodium salt, unchanged through the experiment, since in this form it would pass into the silver salt and would not be extracted by alcohol and ether. We have therefore thought it advisable to repeat this experiment, and our results confirm the conclusion at which Feist arrived. The hydroxy-anhydride when dissolved in excess of $N/10$-sodium carbonate forms a yellow solution, from which the colour slowly disappears; the change from the sodium salt of the hydroxy-anhydride to that of the dibasic acid is complete when the colour has been entirely discharged. The silver salt (mixed with silver carbonate) is then precipitated and decomposed by hydrogen sulphide. The experiment without casein yielded the acid 154—155°, whilst a similar experiment in the presence of casein gave the anhydride melting at 206°. It is therefore evident that the *cis*-form of the acid is unstable, and passes into the anhydride when liberated from its salts.

The Aniline Derivatives of β-Phenylglutaconic Acid.—The semianilide and anil of this acid have been described by Feist and Pomme (*Annalen*, 1909, **370**, 78). The latter melts at 232°, and is described as being soluble in aqueous sodium carbonate without evolution of carbon dioxide.

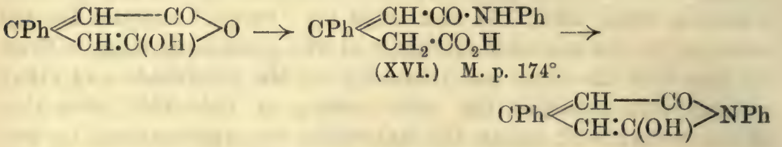
The anil is without question the hydroxy-anil (XIV), since, on titration, it behaves as a monobasic acid and forms alkali salts of formula (XV):



$$\mathrm{CPh}{<}\begin{matrix}\mathrm{CH}\text{---}\mathrm{CO}\\ \mathrm{CH{:}C(OH)}\end{matrix}{>}\mathrm{NPh} \quad \underset{\text{alkali.}}{\overset{\text{acid}}{\rightleftarrows}} \quad \mathrm{CPh}{<}\begin{matrix}\mathrm{CH}\text{---}\mathrm{CO}\\ \mathrm{CH{:}C(ONa)}\end{matrix}{>}\mathrm{NPh}$$

(XIV.) M. p. 232°. (XV.)

The semianilide (XVI) (m. p. 174°) is formed when the hydroxy-anhydride is treated with aniline, and is completely converted into the hydroxy-anil when heated at 150°:



$$\mathrm{CPh}{<}\begin{matrix}\mathrm{CH}\text{---}\mathrm{CO}\\ \mathrm{CH{:}C(OH)}\end{matrix}{>}\mathrm{O} \longrightarrow \mathrm{CPh}{<}\begin{matrix}\mathrm{CH{\cdot}CO{\cdot}NHPh}\\ \mathrm{CH_2{\cdot}CO_2H}\end{matrix} \longrightarrow \mathrm{CPh}{<}\begin{matrix}\mathrm{CH}\text{---}\mathrm{CO}\\ \mathrm{CH{:}C(OH)}\end{matrix}{>}\mathrm{NPh}$$

(XVI.) M. p. 174°.

The neutral solution of the alkali salt of the hydroxy-anil is not transformed into the alkali salt of the semianilide on heating, and it is therefore evident that the form having the mobile hydrogen atom outside the three-carbon system possesses great stability.

The derivatives of β-phenylglutaconic acid may be therefore summarised as follows:

	trans-Acid.	*cis*-Acid.	Hydroxy-anhydride.	Semi-anilide.	Hydroxy-anil.
β-Phenylglutaconic acid... $\mathrm{CO_2H{\cdot}CH{\cdot}CPh(H){\cdot}CH{\cdot}CO_2H}$	154—155°	unstable	206°	174°	232°

The conclusions to be derived from these experiments may be stated in the following way:

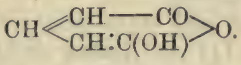
(1) Glutaconic acid exists in one form only, but when the symmetry of the molecule is destroyed, as in, for example, the semianilides, well-defined *cis*- and *trans*-modifications can be isolated.

(2) The β-substituted derivatives of glutaconic acid differ from all the other members of the series in their capacity for anhydride formation. The behaviour of the hydroxy-anils shows that there is a marked tendency in compounds of this type for the mobile hydrogen to remain outside the three-carbon system.

(3) The normal anhydrides of glutaconic acid and of its β-substituted derivatives do not appear to be capable of existence. The hydroxy-anhydrides are characterised by giving intense colours with ferric chloride, which, however, almost immediately disappear. They therefore differ in this respect from the hydroxy-anhydrides of the other members of the series which give no pronounced colours with this reagent.

EXPERIMENTAL.

The Hydroxy-anhydride of Glutaconic Acid (6-*Hydroxy-α-pyrone*),



$$\mathrm{CH}<\begin{matrix}\mathrm{CH}\text{---}\mathrm{CO}\\ \mathrm{CH}:\mathrm{C(OH)}\end{matrix}>\mathrm{O}.$$

This substance, previously described as the normal anhydride, can be prepared by Buchner's method (*Ber.*, 1894, **27**, 881) if acetyl chloride containing some phosphorus trichloride is employed, but is best obtained by boiling the acid (20 grams) with acetic anhydride (30 grams) for half an hour, and distilling the dark red liquid under diminished pressure. The pure anhydride passes over at 152—153°/15 mm. (compare Perkin and Tattersall, Trans., 1905, **87**, 365) and solidifies. It is very sparingly soluble in dry ether, and can be purified by washing with this solvent. It is best recrystallised from benzene, from which it separates in long, slender needles melting at 87°:

0·1709 gave 0·3347 CO_2 and 0·0871 H_2O. C=53·48; H=3·67.

$C_5H_4O_3$ requires C=53·6; H=3·6 per cent.

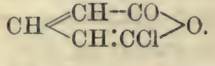
The hydroxy-anhydride dissolves unchanged in cold water, and can be recrystallised from this solvent if the solution is sufficiently concentrated. The aqueous solution gives an intense green coloration with ferric chloride, which changes almost at once to pale brown:

0·2101 required 9·7 c.c. of NaOH solution (1 c.c.=0·00785 gram NaOH).

$C_5H_4O_3$ (monobasic) requires 9·6 c.c.

The neutral solution becomes deep wine-red on keeping, a reaction which appears to be characteristic of all the hydroxy-anhydrides of the glutaconic series. If the neutral solution is acidified the hydroxy-anhydride can be extracted from it with ether. It dissolves in concentrated aqueous potassium hydroxide, forming a deep yellow solution, which slowly becomes colourless on keeping, and when cautiously acidified and extracted by ether yields glutaconic acid (m. p. 137°) as sole product. The same acid is also formed when the hydrolysis of the hydroxy-anhydride is effected by aqueous sodium carbonate in the presence of casein (compare Feist, *Annalen*, 1909, **370**, 54).

The Chloro-anhydride of Glutaconic Acid (6-*Chloro-α-pyrone*),



$$\mathrm{CH}<\begin{matrix}\mathrm{CH}\text{--}\mathrm{CO}\\ \mathrm{CH}:\mathrm{CCl}\end{matrix}>\mathrm{O}.$$

The action of acetyl chloride on glutaconic acid leads to a number of products, different conditions of temperature having a most remarkable effect on the result. The chloro-anhydride is produced when the conditions for the formation of the anhydride recommended by Buchner (*loc. cit.*) are followed, and can be isolated in the following way:

One part of the acid and eight parts of acetyl chloride (Kahlbaum's acetyl chloride II) are heated on the water-bath for forty minutes, when the excess of chloride is evaporated on the water-bath and the residue dissolved in dry ether. The hydroxy-anhydride and unchanged acid are then removed from the ether by shaking it with sodium hydrogen carbonate solution, and the ethereal solution dried and evaporated. The residue solidifies at once, and when dry melts at 27°:

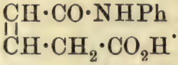
0·2176 gave 0·2387 AgCl. Cl = 27·13.

$C_5H_3O_2Cl$ requires Cl = 27·2 per cent.

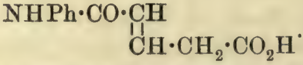
The chloro-anhydride is insoluble in cold alkali, but dissolves on warming, forming the dialkali salt of glutaconic acid. It is also converted into the same acid when boiled with water.

With acetyl chloride at a higher temperature glutaconic acid yields at least three distinct substances having acid properties and containing chlorine. The chief of these is a crystalline compound melting at 73°, which yields an aniline derivative melting at 158°. As the structure of these compounds and their connexion with glutaconic acid is not yet clearly defined, it is proposed to reserve a description of them for a future communication.

The Aniline Derivatives of Glutaconic Acid.

The cis-*Semianilide*, 

$\begin{array}{l}\text{CH·CO·NHPh}\\ \| \\ \text{CH·CH}_2\text{·CO}_2\text{H}\end{array}$.—We have prepared this anilide in benzene solution, and find that after recrystallisation from benzene it melts sharply at 135°. (Found, C = 64·21; H = 5·52. Calc., C = 64·4; H = 5·4 per cent.) The *cis*-semianilide is completely converted into the *trans*-modification on heating at 150° (see below).

The trans-*Semianilide*, 

$\begin{array}{l}\text{NHPh·CO·CH}\\ \qquad\qquad\;\; \| \\ \qquad\qquad\;\text{CH·CH}_2\text{·CO}_2\text{H}\end{array}$.—This modification is best prepared by heating the *cis*-semianilide at 150° for half an hour. The gummy residue yields a crystalline solid when rubbed with ether, which separates from a mixture of benzene and alcohol in small prisms melting at 167°.

It is also formed when glutaconic acid is heated with one molecular proportion of aniline at 150° for half an hour, but is accompanied by other products from which it can be separated only with difficulty. It can be isolated, however, by dissolving the fused mass in ether and shaking the ethereal solution with sodium carbonate. The alkaline extract yields a gum when acidified, from which the semianilide can be isolated by the aid of benzene:

0·1410 gave 0·3320 CO_2 and 0·0720 H_2O. C=64·23; H=5·67.
$C_{11}H_{11}O_3N$ requires C=64·4; H=5·4 per cent.

The other products formed by the action of aniline on glutaconic acid appear to be of high molecular weight; they are still under investigation.

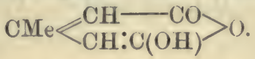
The *dianilide*, NHPh·CO·CH·CH(H)·CH·CO·NHPh, is produced when the chloro-anhydride dissolved in benzene is mixed with a benzene solution containing the requisite quantity (3 molecules) of aniline. Aniline hydrochloride is first precipitated, but the dianilide quickly separates on scratching. The product is then collected, washed with dilute alcohol to remove the aniline salt, and finally recrystallised from dilute alcohol. It forms small needles melting at 228°, and is insoluble in alkali:

0·2488 gave 0·6659 CO_2 and 0·1318 H_2O. C=72·98; H=5·88.
$C_{17}H_{16}O_2N_2$ requires C=72·9; H=5·7 per cent.

β-Methylglutaconic Acid, $CO_2H·CH·CMe(H)·CH·CO_2H$.

The experiments described in the next section show that the first form of the acid to be produced by the action of hydrolysing agents on the hydroxy-anhydride is that melting at 115—116°, and it is therefore this acid which must be regarded as the *cis*-modification, and not the acid melting at 149° as previously supposed (Feist, *Annalen*, 1906, **345**, 78).

The Hydroxy-anhydride of β-Methylglutaconic Acid (*6-Hydroxy-4-methylpyrone*),



$$\mathrm{CMe}<\begin{matrix}\mathrm{CH}\text{——}\mathrm{CO}\\ \mathrm{CH{:}C(OH)}\end{matrix}>\mathrm{O}.$$

Both modifications of β-methylglutaconic acid react with acetyl chloride at the ordinary temperature, and the reaction is quickly completed by warming on the water-bath. The hydroxy-anhydride remains as a crystalline solid when the excess of chloride is evaporated over potassium hydroxide in a desiccator, and can be purified by rubbing with dry ether or by recrystallisation from benzene. The long, flattened needles obtained in this way melted at 90°, that is, 4° higher than the anhydride prepared by Genvresse (*Ann. Chim. Phys.*, 1891, [vi], **24**, 88), by Rogerson and Thorpe (Trans., 1905, **87**, 1691), and by Feist (*Annalen*, 1906, **345**, 84). A direct comparison of the two specimens showed that the anhydride of lower melting point contained traces of the chloro-anhydride (see below), and that it is a matter of some difficulty to obtain the hydroxy-anhydride free from this impurity if the acid is heated with acetyl chloride for more than ten minutes. The anhydride melting at 86° yielded the pure form melting at 90° after being twice recrystallised from benzene:

0·1896 gave 0·3964 CO_2 and 0·0827 H_2O. C=57·02; H=4·85.

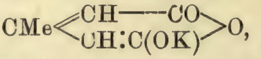
$C_6H_6O_3$ requires C=57·1; H=4·8 per cent.

The hydroxy-anhydride distils at 210°/45 mm., and can be recrystallised from water. The aqueous solution gives an intense purple coloration with ferric chloride, which almost immediately changes to brown. The anhydride dissolves in aqueous sodium carbonate with effervescence, and if the solution is acidified at once the hydroxy-anhydride is reprecipitated:

0·1882 required 7·63 c.c. of NaOH solution (1 c.c.=0·0079 gram NaOH).

$C_6H_6O_3$ (monobasic) requires 7·6 c.c.

The hydroxy-anhydride is very stable, and requires to be heated for some hours with excess of alkali before it is completely hydrolysed to the di-alkali salt of the acid.

The *potassium* salt,  $\mathrm{CMe}<\begin{matrix}\mathrm{CH}\text{——}\mathrm{CO}\\ \mathrm{CH{:}C(OK)}\end{matrix}>\mathrm{O}$, is precipitated when excess of aqueous potassium hydroxide is added to a solution of the hydroxy-anhydride in the dilute alkali. It can be purified by washing with alcohol:

0·2374 gave 0·1244 K_2SO_4. K=23·49.

$C_6H_5O_3K$ requires K=23·8 per cent.

The *silver* salt is a white, crystalline precipitate, which quickly blackens on exposure to light:

0·2280 gave 0·1052 Ag. Ag=46·14.

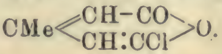
$C_6H_5O_3Ag$ requires Ag=46·4 per cent.

Transformation of the Hydroxy-anhydride into the Acid melting at 115—116°.

The hydroxy-anhydride is mixed with 30 per cent. aqueous potassium hydroxide and warmed to 35°. The mixture is kept at this temperature until the clear solution deposits no potassium salt when cooled and the original yellow colour of the solution has entirely disappeared. It is then diluted with water, acidified, and extracted by ether. The ethereal solution on evaporation gave an acid melting at 112—114°, which after recrystallisation melted at 115—116°.

Feist (*Annalen*, 1909, **370**, 54) tried his "casein" method with the anhydride of *β*-methylglutaconic acid, and obtained the acid melting at 149° as sole product. He therefore concluded that this acid was the one first formed during the hydrolysis of the anhydride, and assigned to it the *cis*-configuration. In view of the experiment with potassium hydroxide described above, we decided to repeat his experiment, using rather more casein than he did. The details of our experiment were similar to those given by him for α-methylglutaconic anhydride (*loc. cit.*, p. 70), only we used excess of *N*/10-sodium carbonate solution and precipitated the silver salt of the acid together with silver carbonate. The acid obtained by the decomposition of the salt melted after recrystallisation at 115—116°. A similar experiment without casein yielded the acid melting at 149°, and this acid is also formed when the hydroxy-anhydride is dissolved in cold water and the solution allowed to remain for some days.

The Chloro-anhydride of β-Methylglutaconic Acid (6-*Chloro*-4-*methyl-α-pyrone*),



$$\mathrm{CMe}<\begin{matrix}\mathrm{CH{-}CO}\\ \mathrm{CH{:}CCl}\end{matrix}>\mathrm{O}.$$

This compound is always formed in small amount when β-methylglutaconic acid is heated with acetyl chloride, and is produced in considerable quantity when one part of the acid and eight parts of the chloride are heated on the water-bath for four hours. It can be isolated by dissolving the residue, freed from excess of chloride, in dry ether, and removing the hydroxy-anhydride by shaking with aqueous sodium bicarbonate. The residue solidifies, and can be purified by recrystallisation from light petroleum. The chloro-anhydride forms slender needles which melt at 43°:

0·2216 gave 0·2189 AgCl. Cl = 24·43.

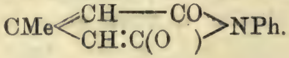
$C_6H_5O_2Cl$ requires Cl = 24·6 per cent.

The chloro-anhydride dissolves slowly when boiled with water, and the acid melting at 149° can be extracted from the solution by ether. When treated with excess of concentrated aqueous potassium hydroxide it is first converted into the potassium salt of the hydroxy-anhydride, and finally into the salt of the *cis*-acid.

The Aniline Derivatives of β-Methylglutaconic Acid.

The *semianilide*, $CO_2H\cdot CH_2\cdot CMe{:}CH\cdot CO\cdot NHPh$, is best prepared from the hydroxy-anhydride and aniline in benzene solution. It is sparingly soluble in benzene, but separates from a large quantity of the solvent in needle clusters melting at 143°. (Found, C = 65·67; H = 5·95. Calc., C = 65·8; H = 5·9 per cent.) The semianilide is completely converted into the hydroxy-anil (see below) when heated at 150°.

The Hydroxy-anil of β-Methylglutaconic Acid (*3-Hydroxy-2-phenyl-5-methyl-*1 : 2-*dihydropyridone*),



$$\mathrm{CMe}{<}\begin{matrix}\mathrm{CH}\text{——}\mathrm{CO}\\ \mathrm{CH{:}C(O\ \ )}\end{matrix}{>}\mathrm{NPh.}$$

This substance is formed when either the *cis*- or the *trans*-modification of β-methylglutaconic acid is heated with aniline. Three grams of the acid are mixed with 2 grams of aniline and heated at 150° for twenty minutes. The resinous product solidifies when rubbed with dry ether, and is obtained in long needles melting at 165° by recrystallisation from alcohol:

0·1660 gave 0·4342 CO_2 and 0·0794 H_2O. C=7·34; H=5·32.

$C_{12}H_{11}O_2N$ requires C=71·6; H=5·5 per cent.

The hydroxy-anil dissolves in alkali carbonate solutions, and is reprecipitated on the addition of acid:

0·2022 required 5·2 c.c. of NaOH solution (1 c.c.=0·0079 gram NaOH).

$C_{12}H_{11}O_2N$ (monobasic) requires 5·1 c.c.

The hydroxy-anil is also formed when the semianilide is heated at 150° for twenty minutes, and can be isolated by rubbing the product with dry ether.

β-Phenylglutaconic Acid, $CO_2H{\cdot}CH{\cdot}CPh(H){\cdot}CH{\cdot}CO_2H$.—We have already stated in the introduction that the best method of preparing this acid is that recommended by Michael, using benzene as the solvent as suggested by Feist. As Feist gives no experimental details, but refers to an Inaugural Dissertation by G. Pomme (Kiel, 1909), which has not been abstracted, it is desirable to give a short account of the method by which this important acid may be prepared in considerable quantity.

Sodium (2·3 grams) is melted under xylene, and brought into a fine state of division by shaking. It is freed from xylene by washing with benzene, and is then suspended in 100 c.c. of benzene and mixed with 16 grams of ethyl malonate. Ethyl phenylpropiolate (17·4 grams) is now added, and the deep yellow solution warmed on the water-bath for six hours, when the benzene is evaporated and the residue mixed with three times its volume of dry ether. The yellow sodium compound,

$$CPh(CO_2Et)_2{\cdot}CHNa{\cdot}CO_2Et,$$

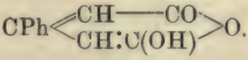
separates completely after twelve hours, and is converted into the acid by hydrolysis with alcoholic potassium hydroxide. The acid melts at 154—155°, and with cold acetyl chloride gives an anhydride which melts at 206°. The *cis*-acid is unstable, and is converted into the anhydride when liberated from its salts.

Ethyl γ-Carbethoxy-β-phenylglutaconate, $CO_2Et{\cdot}CH{\cdot}CPh(H){\cdot}C(CO_2Et)_2$.

This ester, described by Ruhemann and Cunnington (Trans., 1898, **73**, 1015) as a yellow oil, crystallises from dilute alcohol in long, slender, colourless needles, melting at 38°, to a liquid which boils at 221°/15 mm.:

0·1797 gave 0·4244 CO_2 and 0·1024 H_2O. C = 64·45; H = 6·43.
$C_{18}H_{22}O_6$ requires C = 64·7; H = 6·6 per cent.

The Hydroxy-anhydride of β-Phenylglutaconic Acid (6-*Hydroxy-4-phenyl-α-pyrone*),



$\mathrm{CPh}{<}\begin{matrix}\mathrm{CH}\text{——}\mathrm{CO}\\ \mathrm{CH{:}C(OH)}\end{matrix}{>}\mathrm{O}$.

This substance, formerly described as the normal anhydride, is readily prepared by dissolving the acid in warm acetyl chloride, and allowing the solution to cool. The crystals which separate can be purified by recrystallisation from ethyl acetate, and then melt at 206°, as found by Feist:

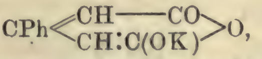
0·1881 gave 0·4833 CO_2 and 0·0714 H_2O. C = 70·07; H = 4·21.
$C_{11}H_8O_3$ requires C = 70·2; H = 4·3 per cent.

The hydroxy-anhydride gives a dark red coloration with ferric chloride in dilute alcohol, and is soluble in alkali carbonate solutions:

0·2178 required 5·8 c.c. NaOH solution (1 c.c. = 0·0079 gram NaOH).
$C_{11}H_8O_3$ (monobasic) requires 5·86 c.c.

The anhydride dissolves in aqueous sodium carbonate, and the sodium salt separates in yellow, glistening plates if excess of the alkali is added.

The *potassium* salt,



$\mathrm{CPh}{<}\begin{matrix}\mathrm{CH}\text{——}\mathrm{CO}\\ \mathrm{CH{:}C(OK)}\end{matrix}{>}\mathrm{O}$, is precipitated when excess of aqueous potassium hydroxide is added to a solution of the hydroxy-anhydride in dilute alkali. It crystallises from alcohol containing a little water in glistening, primrose-yellow plates:

0·2653 gave 0·1016 K_2SO_4. K = 17·17.
$C_{11}H_7O_3K$ requires K = 17·25 per cent.

The *silver* salt precipitated from an aqueous solution of the potassium salt by silver nitrate is a lemon-yellow powder, which rapidly darkens on exposure to light:

0·1292 gave 0·0475 Ag. Ag = 36·71.
$C_{11}H_7O_3Ag$ requires Ag = 36·6 per cent.

The Ethyl Hydrogen Salt of β-Phenylglutaconic Acid, $\mathrm{CO_2Et{\cdot}CH_2{\cdot}CPh{:}CH{\cdot}CO_2H}$.

—This compound is always formed during the etherification of β-phenylglutaconic acid by alcohol and sulphuric acid, and can be extracted from the ethereal solution of the product by aqueous sodium carbonate. It forms slender needles from a mixture of light petroleum and benzene, and melts at 78°:

0·1596 gave 0·3900 $\mathrm{CO_2}$ and 0·0870 $\mathrm{H_2O}$. C = 66·64; H = 6·05.

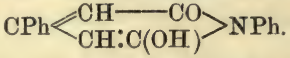
$\mathrm{C_{13}H_{14}O_4}$ requires C = 66·7; H = 6·0 per cent.

The acid ester is slowly converted into the hydroxy-anhydride when distilled.

The Aniline Derivatives of β-Phenylglutaconic Acid.

The *semianilide*, $\mathrm{NHPh{\cdot}CO{\cdot}CH_2{\cdot}CPh{:}CH{\cdot}CO_2H}$, from the hydroxy-anhydride and aniline melts at 174° after recrystallisation from dilute alcohol. It is readily soluble in acetone, and is converted into the hydroxy-anil when heated at 150°.

The Hydroxy-anil of β-Phenylglutaconic Acid (3-*Hydroxy*-2 : 5-*diphenyl*-1 : 2-*dihydropyridone*),



$$\mathrm{CPh}\Big<\begin{matrix}\mathrm{CH}\text{——}\mathrm{CO}\\ \mathrm{CH{:}C(OH)}\end{matrix}\Big>\mathrm{NPh.}$$

This substance, previously described as the anil, is best prepared by heating 3 grams of β-phenylglutaconic acid with 1·4 grams of aniline at 140° for ten minutes, and rubbing the resinous product with dry ether. It crystallises from acetone in colourless needles, which melt at 232°:

0·1836 gave 0·5220 $\mathrm{CO_2}$ and 0·0862 $\mathrm{H_2O}$. C = 77·30; H = 5·08.

$\mathrm{C_{17}H_{13}O_2N}$ requires C = 77·6; H = 4·9 per cent.

The hydroxy-anil dissolves in alkaline carbonate solutions, and is reprecipitated by acids:

0·1915 required 3·65 c.c. NaOH solution (1 c.c. = 0·0079 gram NaOH).

$\mathrm{C_{17}H_{13}O_2N}$ (monobasic) requires 3·7 c.c.

The hydroxy-anil is also formed from the semianilide by heating it at 150° for ten minutes, and can be isolated from the product by means of cold acetone.

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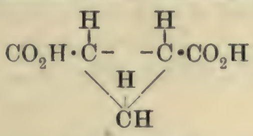
XCI.—*The Chemistry of the Glutaconic Acids. Part IV. The Esters of the Glutaconic Acids.**

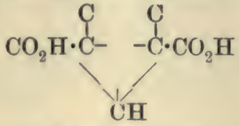
By Norman Bland and Jocelyn Field Thorpe.

It was stated (Trans., 1911, **99**, 2190) that an account of our views respecting the structure of the glutaconic acids would be given in Part IV of this series, but circumstances have arisen which have rendered it necessary to publish this account elsewhere. In the meantime, in order to make the present paper intelligible, it is necessary to state briefly the main conclusions to which we have been led by the experimental evidence already recorded.

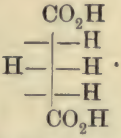
It is assumed that in every mobile † acid of the series there is a static stable state, called the normal state, in which the tautomeric hydrogen atom is attached to the central carbon atom of the three-carbon system. The structure of the normal acid is similar to that of *iso*phthalic acid, and the manner in which the free valency of the two terminal carbon atoms of the system is combined is left an open question, although it is assumed that the free valencies are on the same sides of the two terminal tetrahedrons, and that, for example, glutaconic acid is the meso- or non-resolvable form, thus:



Glutaconic acid.

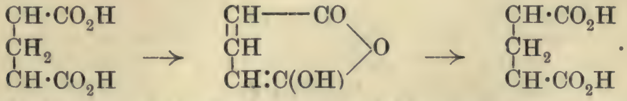


*iso*Phthalic acid.



The normal acids are the so-called *trans*-modifications of the acids of this series.

The dehydration of a mobile acid leads to the formation of the hydroxy-anhydride in which the tautomeric hydrogen atom has passed out of the three-carbon system to the carbonyl system of the acid:



The hydration of the hydroxy-anhydride of glutaconic acid, the example illustrated above, restores the hydrogen atom to the three-carbon system, yielding the normal form of the acid, but it is evident that the formation of the normal acid must be preceded by the production of another acid, called the labile acid, thus:

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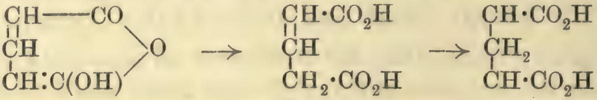
* For abstract, see Proc., 1912, **28**, 56 and 70.

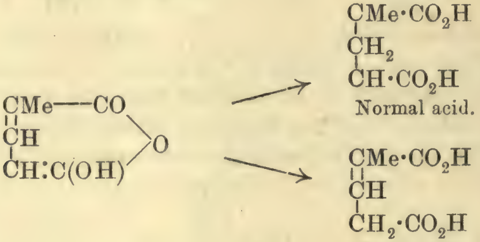
† For the meaning of this phrase, see Trans., 1911, **99**, 2209.



Labile acid.

It is assumed that the labile state of glutaconic acid itself cannot be isolated, because the initial momentum acquired by the hydrogen atom at the moment of its introduction carries it at once into the three-carbon system; but if this initial "spring" is decreased by the presence of an alkyl group on one of the terminal carbon atoms of the three-carbon system, it is possible to cause the hydrogen atom to remain within the carbonyl system by effecting the hydration of the hydroxy-anhydride in the presence of strong alkali or casein.

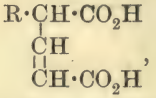
Thus, although the hydroxy-anhydride of, for example, *α*-methylglutaconic acid yields the normal acid on hydration with water, it gives the labile acid when hydrated by strong alkali or by dilute alkali in the presence of casein:



Normal acid.

Labile acid.

The labile acids are the so-called *cis*-forms of the acids of this series. It is assumed that these are the only two forms in which, generally speaking, any given derivative of glutaconic acid can be isolated. Theoretically, the labile acid should exist in maleic and fumaric forms, but the unstable character of these acids causes them to pass into the normal form by all reactions which should give the fumaric modifications. It is also assumed that the true *α*-acids of the type:

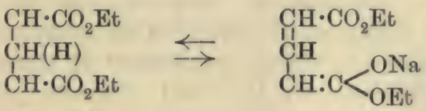


$$\begin{array}{l} R\cdot CH\cdot CO_2H \\ \quad | \\ \quad CH \\ \quad \| \\ \quad CH\cdot CO_2H \end{array},$$

are incapable of isolation, because it has been shown that the presence of the alkyl group throws the hydrogen atom away from the carbon atom affected (compare Trans., 1911, **99**, 2213), and hence the restoration of the hydrogen atom to the α-position would have to take place through the more stable normal state.

Assuming the correctness of this hypothesis, it follows that there are four distinct types of ester, and these may be either tautomeric, desmotropic, or structurally distinct.*

A normal ester of a glutaconic acid such as ethyl glutaconate has the hydrogen within the three-carbon system. When treated with sodium ethoxide it forms the yellow sodium derivative having the metal attached to the oxygen of one of the carbonyl groups, but the decomposition of this compound by water at once restores the hydrogen to the three-carbon system, yielding the original ester: †

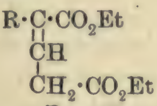


$$\begin{array}{l} CH{\cdot}CO_2Et \\ | \\ CH(H) \\ | \\ CH{\cdot}CO_2Et \end{array} \quad \rightleftarrows \quad \begin{array}{l} CH{\cdot}CO_2Et \\ \| \\ CH \\ | \\ CH{:}C{<}^{ONa}_{OEt} \end{array}$$

Type (*a*).

The first type of ester is therefore the normal type (*a*), having the hydrogen within the three-carbon system. Strictly speaking, ethyl glutaconate is not a tautomeric substance, because neither of the individuals having the hydrogen within the carbonyl system can be isolated.

By substituting the hydrogen atom of one of the α-carbon atoms by alkyl, the chief effect is to retard the re-entrance of the hydrogen atom into the three-carbon system, and to retain it on the carbonyl system not affected by the substituting group. This causes the formation of esters of type (*b*), which are in reality the esters of the labile forms of the acids:



$$\begin{array}{l} R{\cdot}C{\cdot}CO_2Et \\ \quad \| \\ \quad CH \\ \quad | \\ \quad CH_2{\cdot}CO_2Et \end{array}$$

Type (*b*).

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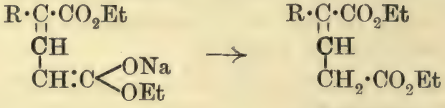
[*] Definitions of these terms indicating the meaning it is intended to convey by their use are desirable. The term *tautomerism* is applied to those substances exhibiting tautomerism of which only one individual can be isolated in the free state. The instability of the second individual is such that equilibrium mixtures are not formed. The term *desmotropism* is applied to those substances exhibiting tautomerism in which equilibrium mixtures of the two forms are produced. The two individuals may or may not be capable of isolation in the free state. The term *structural isomerism* is applied to those substances exhibiting tautomerism of which both individuals are capable of isolation in the free state and which do not form equilibrium mixtures at the ordinary temperature. These terms are, therefore, used to denote degrees of the same kind of phenomenon prevalent under ordinary conditions and at the ordinary temperature.

[†] The statement of Henrich (*Annalen*, 1910, **376**, 122), based on the evidence of the molecular refraction, that glutaconic ester is a mixture of the keto- and enol-forms, has since been corrected (*ibid.*, 1911, **380**, 341).

It is evident that these esters must be those first formed by the decomposition of the sodium compounds of the esters by water, thus:



$$\begin{array}{l} R\cdot C\cdot CO_2Et \\ \;\;\| \\ \;\;CH \\ \;\;| \\ \;\;CH{:}C{<}\begin{smallmatrix}ONa\\OEt\end{smallmatrix} \end{array} \longrightarrow \begin{array}{l} R\cdot C\cdot CO_2Et \\ \;\;\| \\ \;\;CH \\ \;\;| \\ \;\;CH_2\cdot CO_2Et \end{array}$$

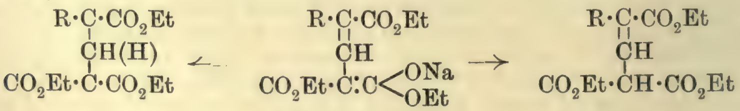
Labile ester.

just as the labile acids are those first produced by the hydration of the hydroxy-anhydrides; but it is to be anticipated that the "spring" of the hydrogen atom when first introduced will lead to the production of an amount of the normal ester depending on the tendency for the hydrogen to re-enter the three-carbon system, that is, on the nature of the substituting group.

The stability of the sodium compounds of these esters must, of course, be dependent on the acid character of the displaced hydrogen. The acidity is determined by the nature of the groups attached to the carbon atom which carries this hydrogen atom, and in those cases in which only one carbethoxyl group is attached to this carbon atom the sodium compound is completely dissociated by water. Although it is probable that in the instance given above the dissociation of the salt leads to a mixture of the esters of the normal and labile acids, it is impossible to furnish any proof, because the labile form is not soluble in alkali, and there is consequently no means of distinguishing between them.

If, however, there are two negative groups attached to the carbon atom carrying the acid hydrogen, the sodium compound of the labile acid is stable in aqueous solution, and can be separated from the normal ester which is produced at the same time.

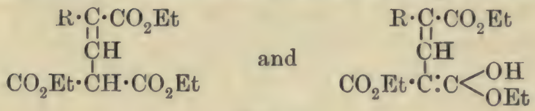
Thus, when the sodium derivative formulated below is added to water, an amount of the normal ester, depending on the tendency of the hydrogen to re-enter the three-carbon system, is produced by the dissociation of the salt, but the whole of the labile ester remains as sodium compound undissociated in the solution, and can be converted into the free labile ester by carbon dioxide (see p. 878):



$$\begin{array}{c} R\cdot C\cdot CO_2Et \\ | \\ CH(H) \\ | \\ CO_2Et\cdot C\cdot CO_2Et \end{array} \longleftarrow \begin{array}{c} R\cdot C\cdot CO_2Et \\ \| \\ CH \\ | \\ CO_2Et\cdot C{:}C{<}\begin{smallmatrix}ONa\\OEt\end{smallmatrix} \end{array} \longrightarrow \begin{array}{c} R\cdot C\cdot CO_2Et \\ \| \\ CH \\ | \\ CO_2Et\cdot CH\cdot CO_2Et \end{array}$$

Normal ester. Sodium compound. Labile ester.

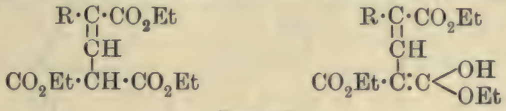
Again, the labile ester of this type may be constituted in two ways. It may be desmotropic, and form equilibrium mixtures of the two individuals (type *c*), in which case the possibility of isolating the two individuals will depend on the rate of change from one form to the other. On the other hand, it may be static under



$$\begin{array}{c} R\cdot C\cdot CO_2Et \\ \| \\ CH \\ | \\ CO_2Et\cdot CH\cdot CO_2Et \end{array} \quad \text{and} \quad \begin{array}{c} R\cdot C\cdot CO_2Et \\ \| \\ CH \\ | \\ CO_2Et\cdot C{:}C{<}\begin{smallmatrix}OH\\OEt\end{smallmatrix} \end{array}$$

Type (*c*).

ordinary conditions as either the enol- or keto-modifications (type *d*), and in this event there will be no tendency to form an



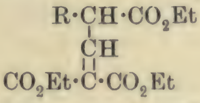
$$\begin{array}{c} R\cdot C\cdot CO_2Et \\ \| \\ CH \\ | \\ CO_2Et\cdot CH\cdot CO_2Et \end{array} \qquad \begin{array}{c} R\cdot C\cdot CO_2Et \\ \| \\ CH \\ | \\ CO_2Et\cdot C{:}C{<}\begin{smallmatrix}OH\\OEt\end{smallmatrix} \end{array}$$

Type (*d*).

equilibrium mixture; the two individuals will have ceased to be either tautomeric or desmotropic, and will have become structurally distinct.

In the following experiments it will be found that all four types of ester have been isolated, and that their stability is entirely determined by the weight of the groups substituting the α- or β-carbon atoms.

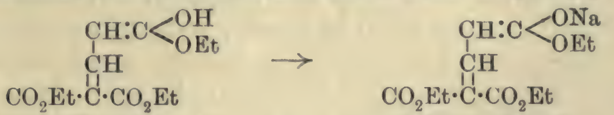
The other possible isomerides of the type:



$$\begin{array}{c} R\cdot CH\cdot CO_2Et \\ | \\ CH \\ \| \\ CO_2Et\cdot C\cdot CO_2Et \end{array}$$

have not been considered, because in all probability they cannot be isolated (compare p. 872).

Esters of this type are, however, formed as sodium compounds when the unsubstituted or β-substituted tricarboxylic esters are treated with alkali (compare this vol., p. 249), but they are strongly acid substances, which are doubtless static esters of type (*d*):



$$\begin{array}{c} CH{:}C{<}\begin{smallmatrix}OH\\OEt\end{smallmatrix} \\ | \\ CH \\ \| \\ CO_2Et\cdot C\cdot CO_2Et \end{array} \longrightarrow \begin{array}{c} CH{:}C{<}\begin{smallmatrix}ONa\\OEt\end{smallmatrix} \\ | \\ CH \\ \| \\ CO_2Et\cdot C\cdot CO_2Et \end{array}$$

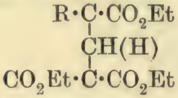
Free ester. Sodium compound.

This is, of course, also the case with the tetracarboxylic ester (ethyl dicarbethoxyglutaconate), and there is no doubt that this substance is static as the enol modification,

$$C(CO_2Et)_2{:}CH\cdot C(CO_2Et){:}C(OH)\cdot OEt.$$

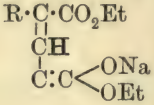
The experiments by which the esters of the four types mentioned above have been isolated, started with a series of tricarboxylic esters substituted in the α-position by methyl, ethyl, and benzyl respectively, a method for the preparation of these substances having been described in Part I of this series (Trans., 1911, **99**, 2197, 2199, and 2200).

When an alcoholic solution of the sodium compound of the methyl * derivative (I) is poured into water, about 90 per cent. of the normal ester (II) is produced, and can be extracted by ether. The remaining 10 per cent. remains as the yellow sodium compound dissolved in the aqueous mother liquor, and the labile ester (III) can be isolated from this by passing carbon dioxide until the colour is discharged:



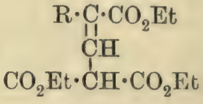
$$\begin{array}{c} R\cdot C\cdot CO_2Et \\ | \\ CH(H) \\ | \\ CO_2Et\cdot C\cdot CO_2Et \end{array}$$

(II.)



$$\begin{array}{l} R\cdot C\cdot CO_2Et \\ \ \ \Vert \\ \ CH \\ \ \ | \\ C{:}C\!<\!\begin{smallmatrix} ONa \\ OEt \end{smallmatrix} \end{array}$$

(I.)



$$\begin{array}{c} R\cdot C\cdot CO_2Et \\ \Vert \\ CH \\ | \\ CO_2Et\cdot CH\cdot CO_2Et \end{array}$$

(III.)

The labile ester (III) is a tautomeric substance, which is slowly but completely extracted from its solution in ether by aqueous potassium hydroxide. The enolic form is unstable, and the action of carbon dioxide on the solution of the alkali salt, even at low temperatures, yields the keto-form only. Even after some months the keto-form gives no colour with ferric chloride, and there is evidently no tendency whatever for this substance to be transformed into an equilibrium mixture of the two individuals.

The normal ester (II) is a stable substance, which is not extracted from its ethereal solution by alkali, but is converted into the enolic sodium compound by the action of alcoholic sodium ethoxide.

When the sodium compound of ester (I), having ethyl in place of methyl, is subjected to the same treatment, it is found that the amount of normal ester (II) is reduced to about 80 per cent., and that the quantity of the labile ester (III) is correspondingly increased.

The labile ester is slowly but completely extracted from its solution in ether by alkali hydroxide, and the separation of the free ester by carbon dioxide at the ordinary temperature causes a complete conversion into the keto-form. It was noticed, however, that when this decomposition was effected at low temperatures the liberated ester gave a pronounced coloration with ferric chloride, but failed to give this reaction after it had been kept at the ordinary temperature for some hours. It is evident, therefore, that, in this case, the enolic form can be isolated at low temperatures, but that at the ordinary temperature it reverts to the stable keto-modification. The keto-ester even after some months fails to give a colour with ferric chloride, and there is evidently no tendency for it to pass into an equilibrium mixture of the two modifications.

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* The formulæ are written with R representing the alkyl group to economise space.

The sodium derivative of the benzyl ester (I) yields with water about equal quantities of the normal ester (II), and an ester which is liberated from the yellow aqueous solution of the sodium derivative by carbon dioxide at the ordinary temperature.

When the ester liberated in this manner is dissolved in ether and shaken with aqueous alkali hydroxide, about 15 per cent. is immediately extracted by alkali, and further treatment with alkali fails to extract more. The extracted solution gives no colour with ferric chloride, but acquires this property after some hours, and a further small amount can then be extracted by shaking with alkali. It is evident, therefore, that the labile ester (III) slowly forms an equilibrium mixture of the two individuals, and that the restoration of equilibrium after the enolic modification has been extracted by alkali is a very slow process.

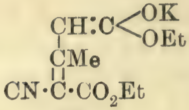
When the solution of the alkali salt is treated with carbon dioxide at low temperatures, an ester is obtained which is almost completely extracted from its solution in ether by aqueous alkali. It gives an intense coloration with ferric chloride, and is without doubt a nearly pure form of the enolic ester. It is fairly stable at the ordinary temperature, but, even under these conditions, slowly reverts to the keto-form, or rather to the equilibrium mixture; this change is very rapid when the oil is heated at the temperature of the water-bath.

It follows, therefore, that the introduction of the benzyl group increases the amount of labile ester formed by the decomposition of the sodium compound by water, and that whereas the corresponding methyl and ethyl derivatives form labile esters in which the keto- and enol-forms are tautomeric at the ordinary temperature, the benzyl derivative yields a labile ester in which definite desmotropism can be detected.

It has been already stated that the greatest effect is produced in the molecule of glutaconic acid by the attachment of an alkyl group to the β-carbon atom, and the next series of experiments were instituted in order to compare tricarboxylic esters of this type with those described above which have the β-position unsubstituted.

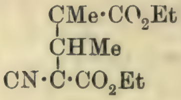
Unfortunately, it is a very difficult matter to prepare tricarboxylic esters of this kind, and it is practically impossible to obtain them in anything like sufficient quantity for the purpose of this comparison.

It was necessary, therefore, to use the corresponding cyanodicarboxylic esters, because it is easy to prepare the methyl, ethyl, and benzyl derivatives from the potassium compound (IV), the preparation of which has been previously described (Trans., 1905, **87**, 1694; compare Proc., 1912, **28**, 51):



$$\begin{array}{l} \mathrm{CH{:}C{<}^{OK}_{OEt}} \\ \quad | \\ \mathrm{CMe} \\ \quad \| \\ \mathrm{CN{\cdot}C{\cdot}CO_2Et} \end{array}$$

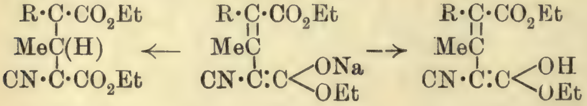
(IV.)



$$\begin{array}{l} \mathrm{CMe{\cdot}CO_2Et} \\ \quad | \\ \mathrm{CHMe} \\ \quad | \\ \mathrm{CN{\cdot}C{\cdot}CO_2Et} \end{array}$$

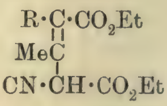
(V.)

The introduction of a methyl group to form the ester (V) confers on the compound properties very similar to those recorded above for the *α*-benzyl derivative; thus the sodium derivative (VI) yields with water about equal quantities of the normal ester (VII), and a sodium derivative in solution which yields the labile ester when decomposed by carbon dioxide. From this labile ester about 20 per cent. can be extracted by aqueous potassium hydroxide, and can be liberated as the enolic form (VIII) by carbon dioxide at low temperatures. The enolic ester gives a deep colour with ferric chloride, and is fairly stable at the ordinary temperature, but it rapidly reverts to the equilibrium mixture at the temperature of the water-bath:



$$\begin{array}{ccccc} \begin{array}{l} \mathrm{R{\cdot}C{\cdot}CO_2Et} \\ \mathrm{MeC(H)} \\ \mathrm{CN{\cdot}C{\cdot}CO_2Et} \end{array} & \longleftarrow & \begin{array}{l} \mathrm{R{\cdot}C{\cdot}CO_2Et} \\ \quad \| \\ \mathrm{MeC} \\ \mathrm{CN{\cdot}C{:}C{<}^{ONa}_{OEt}} \end{array} & \longrightarrow & \begin{array}{l} \mathrm{R{\cdot}C{\cdot}CO_2Et} \\ \quad \| \\ \mathrm{MeC} \\ \mathrm{CN{\cdot}C{:}C{<}^{OH}_{OEt}} \end{array} \end{array}$$

(VII.) (VI.) (VIII.)



$$\begin{array}{l} \mathrm{R{\cdot}C{\cdot}CO_2Et} \\ \quad \| \\ \mathrm{MeC} \\ \mathrm{CN{\cdot}CH{\cdot}CO_2Et} \end{array}$$

(IX.)

The keto-form (IX) of the labile ester gives no colour with ferric chloride immediately after extraction by alkali, but acquires this property after some time. More of the enolic form can then be extracted by alkali, and it is therefore evident that in this case, as with the *α*-benzyl derivative, the keto- and enol-forms of the labile ester are desmotropic.

The esters produced by the entrance of ethyl in place of methyl call for no special comment. In comparison with the methyl derivative a smaller amount of the normal ester is produced, the enol-form of the labile ester possesses greater stability, and the rate at which the equilibrium mixture of the keto- and enol-forms of the labile ester is restored is diminished.

The replacement of the metal in the potassium compound by benzyl leads to an ester from the sodium derivative (VI) of which about 30 per cent. of the normal ester (VII) is obtained by the action of water (see p. 874).

The decomposition of the yellow aqueous solution at low temperatures by carbon dioxide leads to the formation of the enolic form (VIII) alone.

This ester is completely extracted from its solution in ether by aqueous potassium hydroxide, and gives a deep colour with ferric chloride. It is a very stable substance, and is unchanged after keeping for some months at the ordinary temperature. When distilled it passes slowly into the keto-form of the labile ester, from which it can be regenerated by the action of alcoholic sodium ethoxide. The keto-form of the labile ester (IX) is also a stable substance, and shows no tendency to pass into an equilibrium mixture of the two forms.

The sodium derivatives were prepared in alcoholic solution, and it is evident that in this condition they are not ionised, because the action of an alkyl iodide causes complete conversion into the corresponding alkyl derivatives. Ionisation therefore ensues only when the alcoholic solution is mixed with water, and a certain amount of the ionised sodium derivative is then hydrolytically dissociated, yielding free alkali and the normal ester having the hydrogen atom within the three-carbon system.

There is no doubt that the dissociation of the sodium compounds in this manner is primarily determined by the tendency for the hydrogen atom to pass into the three-carbon system, and is therefore dependent on the nature of the groups attached to the carbon atoms of the three-carbon system.

Actually, the extent of the dissociation is determined by the amount of free alkali generated in the solution, and the process is ultimately stopped when sufficient alkali has been produced to establish equilibrium between the undissociated sodium compound and the free alkali generated.

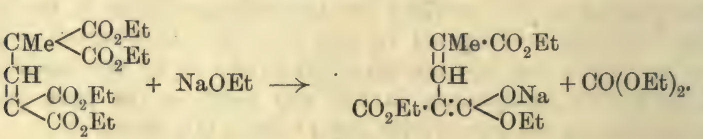
It follows that the amount of alkali required to check the process of dissociation, and therefore the amount of normal ester formed, must depend on the tendency for the hydrogen atom in the particular instance investigated to pass into the three-carbon system. It also follows that the normal esters produced by the dissociation of the sodium compounds in this way must be the pure normal esters, and are not mixed with any of the labile esters.

The labile esters are precipitated from the aqueous solution of the sodium compounds, containing sufficient free alkali to check further dissociation, by the action of carbon dioxide. This reagent must, in the first instance, attack the free alkali, and it might be anticipated that the replacement of the sodium hydroxide in the solution by sodium bicarbonate would cause a further dissociation of the sodium compound, and thus produce more of the normal ester. This is, however, not the case, because experiment shows that the whole of the free alkali can be converted into bicarbonate without any further dissociation occurring, and that the precipitation of the labile ester commences only after all the free alkaline hydroxide has been removed. It follows, therefore, that the labile esters prepared in this manner are the pure labile esters, and are not mixed with any of their normal isomerides.

In this paper it is shown that the amount of normal ester formed by the dissociation of the sodium compounds of the esters decreases with the weight of the groups attached to the carbon atoms of the three-carbon system, and that the greatest effect is produced by the entrance of a group on the β-carbon atom of this system. In general terms this may be expressed by saying that the initial "spring" of the hydrogen atom when introduced either by the hydrolytic dissociation of the sodium compounds or by the hydration of the hydroxy-anhydrides of the acids decreases with the weight of the groups occupying the carbon atoms of the three-carbon system, or, in other words, the increase in the weight of the groups occupying the carbon atoms of the three-carbon system decreases the power of movement of the hydrogen atom from one system to the other.

Further experimental proof of the truth of this statement is supplied by the study of the tricarboxylic esters and cyanodicarboxylic esters described in this paper.

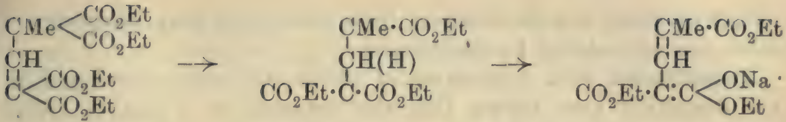
In Part I of this series (Trans., 1911, **99**, 2191) it was shown that the esters of substituted glutaconic acids, which have the tautomeric hydrogen atom displaced, react with alcoholic sodium ethoxide, yielding ethyl carbonate and an ester containing the tautomeric hydrogen atom; thus ethyl *αγ*-dicarbethoxy-*α*-methylglutaconate, in which the hydrogen atom is displaced, reacts with sodium ethoxide, yielding ethyl carbonate and the sodium compound of ethyl *γ*-carbethoxy-*α*-methylglutaconate:



$$\begin{matrix}\mathrm{CMe}{<}\begin{smallmatrix}\mathrm{CO_2Et}\\ \mathrm{CO_2Et}\end{smallmatrix}\\ | \\ \mathrm{CH}\\ \| \\ \mathrm{C}{<}\begin{smallmatrix}\mathrm{CO_2Et}\\ \mathrm{CO_2Et}\end{smallmatrix}\end{matrix} + \mathrm{NaOEt} \longrightarrow \begin{matrix}\mathrm{CMe{\cdot}CO_2Et}\\ \| \\ \mathrm{CH}\\ | \\ \mathrm{CO_2Et{\cdot}C{:}C}{<}\begin{smallmatrix}\mathrm{ONa}\\ \mathrm{OEt}\end{smallmatrix}\end{matrix} + \mathrm{CO(OEt)_2}.$$

It was also shown that the rate of this change decreased with the increase in the weight of the group occupying the *α*-carbon atom, and that, for example, when benzyl displaced methyl in the above ester the change from the tetracarboxylic ester to the tricarboxylic ester required twelve times as long for completion.

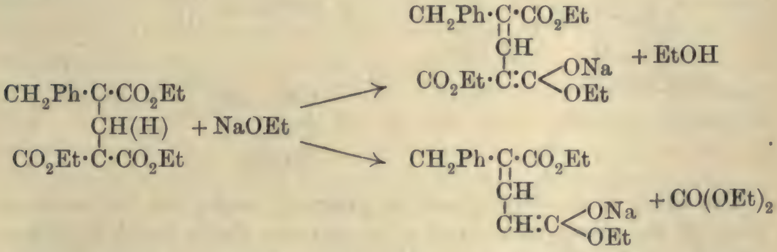
It is necessary here to emphasise the conclusion drawn from the previous experiments that the formation of the sodium derivative in the above instance is a secondary reaction, and that the amount formed in any given time is entirely determined by the tendency for the ester to acquire the tautomeric hydrogen atom. In other words, it is the normal ester which is first formed, and this subsequently yields the sodium derivative by interaction with sodium ethoxide:



$$\begin{array}{l}\mathrm{CMe{<}}{\scriptstyle\begin{array}{l}\mathrm{CO_2Et}\\ \mathrm{CO_2Et}\end{array}}\\ \mathrm{CH}\\ \mathrm{C{<}}{\scriptstyle\begin{array}{l}\mathrm{CO_2Et}\\ \mathrm{CO_2Et}\end{array}}\end{array} \longrightarrow \begin{array}{c}\mathrm{CMe{\cdot}CO_2Et}\\ \mathrm{CH(H)}\\ \mathrm{CO_2Et{\cdot}C{\cdot}CO_2Et}\end{array} \longrightarrow \begin{array}{c}\mathrm{CMe{\cdot}CO_2Et}\\ \mathrm{CH}\\ \mathrm{CO_2Et{\cdot}C{:}C{<}}{\scriptstyle\begin{array}{l}\mathrm{ONa}\\ \mathrm{OEt}\end{array}}\end{array}$$

It therefore follows that the rate of conversion of the normal form of a tricarboxylic ester into its enolic sodium derivative by alcoholic sodium ethoxide will depend on the nature of the group or groups attached to the carbon atom of the three-carbon system.

Experiment shows that when the benzyl group is attached to the *α*-carbon atom the rate of formation of the sodium derivative is decreased to such an extent that a portion of the ester reacts as if it did not contain a tautomeric hydrogen atom, and yields ethyl carbonate and the sodium compound of the dicarboxylic ester, thus:



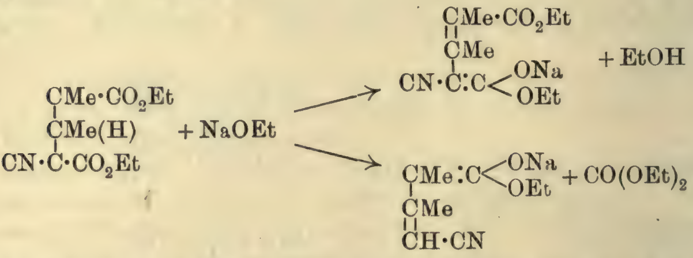
$$\begin{array}{c}\mathrm{CH_2Ph{\cdot}C{\cdot}CO_2Et}\\ \mathrm{CH(H)}\\ \mathrm{CO_2Et{\cdot}C{\cdot}CO_2Et}\end{array} + \mathrm{NaOEt} \begin{array}{l}\nearrow \begin{array}{c}\mathrm{CH_2Ph{\cdot}C{\cdot}CO_2Et}\\ \mathrm{CH}\\ \mathrm{CO_2Et{\cdot}C{:}C{<}}{\scriptstyle\begin{array}{l}\mathrm{ONa}\\ \mathrm{OEt}\end{array}}\end{array} + \mathrm{EtOH}\\ \searrow \begin{array}{c}\mathrm{CH_2Ph{\cdot}C{\cdot}CO_2Et}\\ \mathrm{CH}\\ \mathrm{CH{:}C{<}}{\scriptstyle\begin{array}{l}\mathrm{ONa}\\ \mathrm{OEt}\end{array}}\end{array} + \mathrm{CO(OEt)_2}\end{array}$$

This secondary reaction must be due to a tendency for the ester to acquire a hydrogen atom more "mobile" than the one present in it, and the amount of the sodium compound of the dicarboxylic ester formed in this manner is dependent on the mobility of the hydrogen atom contained in the tricarboxylic ester.

The amount formed is difficult to estimate with any degree of accuracy, because, in the first place, it is necessary to be certain that the experiment has been carried to completion, that is to say, there is no sodium ethoxide remaining in solution, but that the whole of the metal has been partitioned between the sodium compounds of the tricarboxylic and dicarboxylic esters.

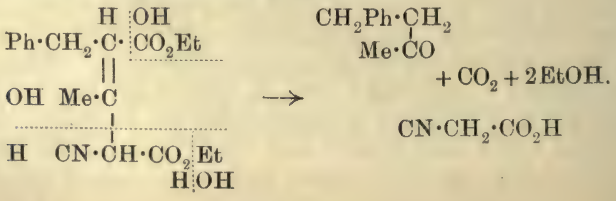
Again, the sodium compounds of the dicarboxylic esters are at once dissociated by water, and they are therefore obtained mixed with the normal esters of the tricarboxylic acids, which are formed by the same process, and can only be separated from them by fractional distillation. In the actual instance of the *α*-benzyl derivative mentioned above, the amount of the dicarboxylic ester is so small (about 7 per cent.) that it cannot be isolated in this manner, and it is necessary to again treat the mixture of normal tricarboxylic ester and dicarboxylic ester with alcoholic sodium ethoxide, remove the labile ester, and again repeat the process before an ester can be obtained from which the pure dicarboxylic ester can be isolated by distillation.

Experiments with derivatives of glutaconic ester substituted in the β-position have shown that the entrance of a methyl group on the β-carbon atom produces, roughly speaking, the same effect as the attachment of a benzyl group to the α-carbon atom. It is therefore to be expected that ethyl α-cyano-αβ-dimethylglutaconate would behave in much the same manner as the α-benzyl-tricarboxylic ester towards sodium ethoxide. This is shown to be the case, because the dimethyl ester yields about 10 per cent. of the sodium compound of the cyano-ester under the same experimental conditions:



The effect of an ethyl group in place of methyl on the α-carbon atom of the above compound is to increase the amount of cyano-ester to about 12 per cent., whilst the presence of a benzyl group in this position so far hinders the movement of the hydrogen atom from one system to the other that an amount of cyano-ester corresponding with 20 per cent. of the cyano-dicarboxylic ester can be obtained by the action of sodium ethoxide.

Attention was drawn in Part I of this series (Trans., 1911, **99**, 2194) to the ease with which certain highly substituted derivatives of glutaconic ester, containing the tautomeric hydrogen atom, undergo fission through the agency of alkali, and it was shown that this tendency increased with the weight of the groups contained in the ester. This property is well illustrated by the behaviour of ethyl α-cyano-γ-benzyl-β-methylglutaconate, for when an alkaline solution of the enolic form of this ester is warmed it is converted into benzylacetone and the sodium salt of cyanoacetic acid. The reaction may be represented by the scheme:



α-Benzyl-β-methylglutaconic acid and the corresponding derivative of dihydroxypyridine will be described in another communication.

EXPERIMENTAL.

Ethyl Carbethoxy-α-methylglutaconate.

The ester described under this name in the previous paper (Trans., 1911, **99**, 2197) was prepared from its yellow sodium compound by the action of dilute hydrochloric acid, and was therefore a mixture of the normal and labile esters. The two constituents may be readily separated in the following way: Fifty-four grams of the mixed esters are converted into the enolic sodium compound by an alcoholic solution of sodium ethoxide containing 4·6 grams of sodium dissolved in 60 c.c. of alcohol, and the deep yellow solution is poured into twice its volume of cold water. The oil which separates is extracted by shaking the solution three successive times with ether, and is then distilled. It boils at 182°/22 mm., is not extracted from its solution in ether by 10 per cent. aqueous potassium hydroxide, and does not give a coloration with ferric chloride. It is therefore *normal ethyl carbethoxy-α-methylglutaconate*,

$$CO_2Et\cdot CMe\cdot CH(H)\cdot C(CO_2Et)_2:$$

0·2265 gave 0·4742 CO_2 and 0·1475 H_2O. C=57·13; H=7·23.

$C_{13}H_{20}O_6$ requires C=57·3; H=7·4 per cent.

The weight of the normal ester formed in this manner is 48 grams, or about 90 per cent. of the ester treated.

Labile ethyl carbethoxy-α-methylglutaconate,

$$CO_2Et\cdot CMe{:}CH\cdot CH(CO_2Et)_2,$$

is precipitated as an oil when carbon dioxide is passed into the yellow aqueous solution left after extracting the normal ester in the above experiment, and is extracted by ether. It is a fairly mobile oil closely resembling the normal ester in appearance, and boils at about the same temperature, that is, at 184°/24 mm.:

0·2080 gave 0·4346 CO_2 and 0·1354 H_2O. C=56·98; H=7·24.

$C_{13}H_{20}O_6$ requires C=57·3; H=7·4 per cent.

The ester differs from the normal ester in being slowly, but completely, extracted from its solution in ether by 10 per cent. aqueous potassium hydroxide. The yellow solution thus formed again yields the ester when treated with carbon dioxide, and it is evident that the liberated ester is the same keto-form since it gives no colour with ferric chloride. The rapid change from the enol- to the keto-form which is indicated by this experiment is not affected when the ester is liberated at low temperatures. There is consequently no tendency for the labile ester to form an equilibrium mixture of the two individuals, and even after keeping for some months it fails to give any colour reaction with ferric chloride.

Ethyl Carbethoxy-α-ethylglutaconate.

In this case, also, the ester previously described (*loc. cit.*, p. 2199) is a mixture of the normal and labile esters, and these can be separated in the same manner as that described for the α-methyl derivative. From 56 grams of the mixed esters and 4·6 grams of sodium in 60 c.c. of alcohol, 45 grams of *normal ethyl carbethoxy-α-ethylglutaconate*, $CO_2Et\cdot CEt\cdot CH(H)\cdot C(CO_2Et)_2$, were obtained on pouring the yellow solution into water, that is, about 80 per cent. of the ester used; it distils at 180°/20 mm.:

0·1932 gave 0·4156 CO_2 and 0·1320 H_2O. C = 58·67; H = 7·59.
$C_{14}H_{22}O_6$ requires C = 58·7; H = 7·7 per cent.

The ester is not extracted from its solution in ether by aqueous alkali, and does not give a colour reaction with ferric chloride.

Labile ethyl carbethoxy-α-ethylglutaconate,

$CO_2Et\cdot CEt{:}CH\cdot CH(CO_2Et)_2$,

is precipitated as an oil when carbon dioxide is passed into the yellow aqueous mother liquor from the above experiment. It boils at 181°/18 mm., and closely resembles the normal ester in appearance, but is slowly extracted from its solution in ether by aqueous alkali:

0·2153 gave 0·4621 CO_2 and 0·1474 H_2O. C = 58·53; H = 7·61.
$C_{14}H_{22}O_6$ requires C = 58·7; H = 7·7 per cent.

The labile ester liberated from the alkaline solution of the potassium compound by carbon dioxide at the ordinary temperature is evidently the keto-form, since it gives no coloration with ferric chloride. It follows that a complete change from the enol- to the keto-modification takes place at the moment the ester is liberated from its alkali compound. If, however, the treatment with carbon dioxide is carried out at a lower temperature, that is, by cooling the solution of the alkali compound by ice and salt, an ester is obtained which gives a red colour reaction with ferric chloride, and must therefore contain some of the enolic modification. The ester loses the property of giving this colour reaction after it has remained for some hours at the ordinary temperature, and almost immediately if it is warmed on the water-bath, showing that a rapid change from the enol- to the keto-form takes place under these conditions. The labile ester does not form an equilibrium mixture on long keeping.

Ethyl Carbethoxy-α-benzylglutaconate.

Since the ester described under this name in the preceding paper (*loc. cit.*, p. 2200) was prepared by the action of dilute hydrochloric acid on the solution of the yellow sodium compound, it follows that it was a mixture of the normal ester with the two desmotropic forms of the labile ester. The normal ester can be readily separated from this mixture, but it is only possible by the method used to obtain the two desmotropic forms in a partial state of purity owing to the rapid formation of an equilibrium mixture of the two individuals.

Normal Ethyl Carbethoxy-α-benzylglutaconate, $CO_2Et{\cdot}C(CH_2Ph){\cdot}CH(H){\cdot}C(CO_2Et)_2$. —From 70 grams of the tricarboxylic ester, 4·6 grams of sodium, and 60 c.c. of alcohol, 38 grams of normal ester were regenerated by the action of water in the way already described. Allowing for the small quantity of the dicarboxylic ester formed at the same time (see below), this represents about 50 per cent. of the ester used. It boils at 218°/22 mm.:

0·2137 gave 0·5116 CO_2 and 0·1350 H_2O. C = 65·28; H = 7·04.
$C_{19}H_{24}O_6$ requires C = 65·5; H = 6·9 per cent.

The ester is not extracted from its solution in ether by aqueous alkali, and does not give a colour reaction with ferric chloride.

Labile Ethyl Carbethoxy-α-benzylglutaconate, $CO_2Et{\cdot}C(CH_2Ph){:}CH{\cdot}CH(CO_2Et)_2$. —A mixture of the keto- and enol-forms of this ester is precipitated when carbon dioxide is passed into the yellow solution of the sodium compound left after extracting the normal ester, and can be separated by ether. It boils at 222°/18 mm., that is, a few degrees higher than the normal ester:

0·2094 gave 0·5008 CO_2 and 0·1322 H_2O. C = 65·22; H = 7·04.
$C_{19}H_{24}O_6$ requires C = 65·5; H = 6·9 per cent.

This ester probably represents with fair accuracy the equilibrium mixture of the two individuals under ordinary conditions. It gives a purple coloration with ferric chloride, and when shaken in ethereal solution with 10 per cent. aqueous potassium hydroxide about 15 per cent. is quickly extracted as the yellow potassium compound. The ethereal solution immediately after extraction in this manner gives no coloration with ferric chloride, but acquires this property after some minutes; after the ethereal solution has been kept for some hours it gives a marked colour reaction with ferric chloride, and more of the enolic form can then be extracted by aqueous alkali. The restoration of equilibrium in ethereal solution is, however, slow, but is quickly effected at the temperature of the water-bath. It was not found possible to isolate the pure keto-form giving no colour reaction with ferric chloride.

The alkaline solution of the yellow potassium compound deposits an oil when treated with carbon dioxide at low temperatures, which gives an intense purple coloration with ferric chloride, and is almost completely re-extracted from its solution in ether by aqueous alkali. It is therefore an almost pure form of the enol-, mixed with a small amount of the keto-modification.

The colour reaction with ferric chloride slowly decreases in intensity when this ester is kept at the ordinary temperature, until finally the equilibrium mixture is again restored. The change is more rapid at the temperature of the water-bath, and is quickly completed when the ester is distilled under diminished pressure. In the latter operation some of the ester is also converted into the pyrone derivative in the manner already described (*loc. cit.*, p. 2201), and experiment shows that it is this ester only which is transformed into the pyrone derivative, and that the normal ester distils unchanged.

Ethyl a-Benzylglutaconate, $CO_2Et\cdot C(CH_2Ph)\cdot CH(H)\cdot CH\cdot CO_2Et$.

This ester is formed in small amount by the elimination of a carbethoxyl group as ethyl carbonate in the manner described on pp. 881, 888, and is contained in the fraction of lower boiling point from the normal ester. The amount formed in one operation is too small to be isolated in a pure condition, but if the normal tricarboxylic ester containing the dicarboxylic ester is again treated with alcoholic sodium ethoxide a further amount of the former will be removed as the labile ester, and will at the same time be converted partly into the dicarboxylic ester. The ester obtained by pouring the alcoholic solution of the sodium derivatives into water will therefore contain a largely increased proportion of the dicarboxylic ester.

A repetition of this operation a third time yields the dicarboxylic ester in a fairly pure condition, and it can then be easily obtained pure by fractional distillation. It is a fairly mobile oil, which boils at 180°/20 mm.:

0·2013 gave 0·5123 CO_2 and 0·1304 H_2O. C=69·43; H=7·21.

$C_{16}H_{20}O_4$ requires C=69·6; H=7·2 per cent.

The ester gives no coloration with ferric chloride, and is not extracted from its solution in ether by aqueous alkali. It is almost certainly a mixture of the normal and labile esters, but at present we have no means of distinguishing between these forms of the dicarboxylic esters. The ester is converted into α-benzylglutaconic acid on hydrolysis.

Ethyl α-Cyano-βγ-dimethylglutaconate.

The ester described in the former paper (Trans., 1905, **87**, 1695) is the pure normal ester, $CO_2Et{\cdot}CMe{\cdot}CMe(H){\cdot}C(CN){\cdot}CO_2Et$. It was prepared by the action of methyl iodide on the potassium compound, $CO_2Et{\cdot}CHK{\cdot}CMe{:}C(CN){\cdot}CO_2Et$ (compare Proc., 1912, **28**, 51), and experiment shows that under these conditions the hydrogen atom remains entirely within the three-carbon system.

This is to be expected when it is remembered that the labile form of the ester has the structure $CO_2Et{\cdot}CMe{:}CMe{\cdot}CH(CN){\cdot}CO_2Et$, and that the formation of this ester from the methylated potassium compound involves the passing of the mobile hydrogen atom through the three-carbon system. It therefore remains in its more stable position within this system. The normal ester is not extracted from its solution in ether by aqueous potassium hydroxide, and gives no coloration with ferric chloride.

Labile ethyl α-cyano-βγ-dimethylglutaconate,

$$CO_2Et{\cdot}CMe{:}CMe{\cdot}CH(CN){\cdot}CO_2Et,$$

may be obtained as the equilibrium mixture of the keto- and enol-forms in the following way: Forty-eight grams of the normal ester are added to a solution of 4·6 grams of sodium in 60 c.c. of alcohol, and the deep yellow solution is then poured into twice its volume of water. Twenty-eight grams of regenerated normal ester is extracted from this by ether, that is to say, about 50 per cent. of the ester used when allowance is made for the small quantity of ethyl γ-cyano-αβ-dimethylcrotonate (see below) which is formed at the same time. The labile ester is precipitated as an oil when carbon dioxide is passed into the yellow aqueous solution, and can be extracted by ether. It boils at 171°/25 mm., and closely resembles the normal ester in appearance:

0·1987 gave 0·4373 CO_2 and 0·1321 H_2O. C = 60·05; H = 7·39.
$C_{12}H_{17}O_4N$ requires C = 60·2; H = 7·1 per cent.

The ester prepared in this manner gives a deep red coloration with ferric chloride, and when it is dissolved in ether and shaken with 10 per cent. aqueous potassium hydroxide the enol portion of the equilibrium mixture is extracted as the yellow potassium compound. The ethereal solution gives no colour reaction with ferric chloride if tested immediately after extraction in this manner, but acquires this property after a few minutes. The intensity of this colour reaction increases, and ultimately a further quantity of the enol-form can be extracted by aqueous alkali. The restoration of equilibrium is very slow in ethereal solution at the ordinary temperature, but is rapidly effected at the temperature of the water-bath.

The alkaline solution of the potassium compound yields the enolic ester in an almost pure condition when it is treated with carbon dioxide at low temperatures (ice and salt). Its purity is shown by the fact that it is almost completely extracted from its solution in ether by aqueous alkali. The ester gives an intense red colour with ferric chloride, but slowly passes into the equilibrium mixture at the ordinary temperature, and this change is rapidly completed when the ester is distilled. Judging from the amount extracted from the distilled ester by alkali, the equilibrium mixture contains about 20 per cent. of the enol-form.

*Ethyl γ-Cyano-αβ-dimethylcrotonate,**
$CN{\cdot}CH{:}CMe{\cdot}CHMe{\cdot}CO_2Et$ (or $CN{\cdot}CH_2{\cdot}CMe{:}CMe{\cdot}CO_2Et$).

This ester is produced in precisely the same manner as ethyl α-benzylglutaconate, the preparation of which is described on p. 886, and can be isolated in the same way. It is a mobile liquid boiling at 139°/18 mm.:

0·1983 gave 0·4660 CO_2 and 0·1376 H_2O. C = 64·14; H = 7·73.

$C_9H_{13}O_2N$ requires C = 64·7; H = 7·8 per cent.

The ester is hydrolysed to a mixture of αβ-dimethylglutaconic acid and 2:6-dihydroxy-4:5-dimethylpyridine (Trans., 1905, **87**, 1696) by hydrochloric acid.

Ethyl α-Cyano-β-methyl-γ-ethylglutaconate.

The ester prepared from the potassium compound and ethyl iodide (Trans., 1905, **87**, 1708) is the pure normal ester,

$CO_2Et{\cdot}CEt{\cdot}CMe(H){\cdot}C(CN){\cdot}CO_2Et$;

it does not give a colour reaction with ferric chloride, and is not extracted from its solution in ether by aqueous alkali.

Labile Ethyl α-Cyano-β-methyl-γ-ethylglutaconate, $CO_2Et{\cdot}CEt{:}CMe{\cdot}CH(CN){\cdot}CO_2Et$. —This ester can be isolated as the equilibrium mixture of the two desmotropic individuals in the same manner as the corresponding dimethyl derivative already described. From 50 grams of the normal ester, 24 grams are regenerated when the alcoholic solution of the sodium compound is mixed with water. The yellow solution when treated with carbon dioxide deposits the equilibrium mixture of the labile ester as an oil which distils at 168°/22 mm.:

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* Since this cyano-ester and others of the same type are produced by the action of sodium ethoxide, their structures are probably best represented by the expression $CN{\cdot}CH{\cdot}CMe(H){\cdot}CR{\cdot}CO_2Et$.

0·1983 gave 0·4465 CO_2 and 0·1364 H_2O. $C=61·41$; $H=7·64$.
$C_{13}H_{19}O_4N$ requires $C=61·7$; $H=7·5$ per cent.

The equilibrium mixture gives a purple coloration with ferric chloride, and is extracted to the extent of about 25 per cent. by aqueous alkali. The ethereal solution extracted in this manner gives no colour reaction with ferric chloride, but the restoration of equilibrium between the two individuals causes it to give this reaction after some time; more of the enol-form can then be extracted by alkali. It was noticed that the restoration of equilibrium in ethereal solution at the ordinary temperature took place more slowly than with the dimethyl derivative.

A pure form of the enol individual is precipitated when carbon dioxide is passed into the strongly alkaline solution of the potassium at low temperatures. It gives a deep purple coloration with ferric chloride, and is only slowly converted into the equilibrium mixture at the ordinary temperature; distillation under diminished pressure rapidly completes this change.

Ethyl γ-Cyano-β-methyl-α-ethylcrotonate,

$CN\cdot CH{:}CMe\cdot CEt\cdot CO_2Et$ (or $CN\cdot CH_2\cdot CMe{:}CEt\cdot CO_2Et$).

This ester is always formed in small quantity in the experiment described above, and is mixed with the normal ester. It can be obtained in sufficient quantity by repeating the process three times with the regenerated normal ester, and can then be prepared in a pure condition by fractionation; it is a mobile liquid boiling at 141°/20 mm.:

0·1973 gave 0·4787 CO_2 and 0·1491 H_2O. $C=66·18$; $H=8·41$.
$C_{10}H_{15}O_2N$ requires $C=66·3$; $H=8·3$ per cent.

The ester yields β-methyl-α-ethylglutaconic acid and 2:6-dihydroxy-4-methyl-5-ethylpyridine (Trans., 1905, **87**, 1709) when hydrolysed by hydrochloric acid.

Normal Ethyl α-Cyano-γ-benzyl-β-methylglutaconate,

$CO_2Et\cdot C(CH_2Ph)\cdot CMe(H)\cdot C(CN)\cdot CO_2Et$.

The normal ester is produced by the action of benzyl chloride on the potassium compound of ethyl α-cyano-β-methylglutaconate under the same conditions as those employed in the preparation of the methyl and ethyl derivatives (Trans., 1905, **87**, 1695 and 1708). The interaction proceeds quickly, and is finished after heating for one hour on the water-bath. The ester distils at 220°/18 mm. as a viscid, colourless oil:

0·2014 gave 0·5076 CO_2 and 0·1200 H_2O. C = 68·74; H = 6·62.

$C_{18}H_{21}O_4N$ requires C = 68·6; H = 6·7 per cent.

The normal ester gives no colour reaction with ferric chloride, and is not extracted from its solution in ether by aqueous alkali.

Labile Ethyl α-Cyano-γ-benzyl-β-methylglutaconate,
$CO_2Et\cdot C(CH_2Ph){:}CMe\cdot CH(CN)\cdot CO_2Et$.

Both keto- and enol-forms of this ester can be isolated in the following way: Seventy-three grams of the normal ester are mixed with a solution containing 5·3 grams of sodium dissolved in 70 c.c. of alcohol, and the yellow solution, after remaining for one hour at the ordinary temperature, is poured into twice its volume of water. Ether extracts 29 grams of regenerated normal ester from this solution, leaving a yellow aqueous mother liquor, from which a mixture of the two individuals of the labile ester are precipitated by carbon dioxide at the ordinary temperature. When the ethereal solution of this mixture is shaken with a 10 per cent. solution of potassium hydroxide, the enol-modification is extracted, and the extracted solution yields the pure *keto-modification* on evaporation. It boils at 221°/18 mm. as a viscid, colourless oil:

0·1895 gave 0·4758 CO_2 and 0·1126 H_2O. C = 68·47; H = 6·60.

$C_{18}H_{21}O_4N$ requires C = 68·6; H = 6·7 per cent.

The pure keto-ester gives no colour reaction with ferric chloride, and is not extracted from its solution in ether by aqueous alkali. After distillation a faint colour is produced by ferric chloride, but the presence of the enol-form could not be detected by extraction with alkali. The production of this colour is probably due to the formation of traces of the dihydroxypyridine derivative, and not to the change from the keto- to the enol-form at the temperature of distillation.

The Enol-modification, $CO_2Et\cdot C(CH_2Ph){:}CMe\cdot C(CN){:}C(OH)OEt$. —This form is precipitated as an oil when carbon dioxide is passed into a well-cooled solution of the potassium compound in excess of alkali. It is a viscid liquid, which is completely extracted from its solution in ether by aqueous alkali, and gives an intense purple coloration with ferric chloride:

0·2455 gave 0·6120 CO_2 and 0·1550 H_2O. C = 68·01; H = 7·02.

$C_{18}H_{21}O_4N$ requires C = 68·6; H = 6·7 per cent.

The enolic modification is quite stable under ordinary temperature conditions, but when rapidly distilled under diminished pressure boils at 235°/18 mm., and is converted to the extent of about

50 per cent. into the keto-modification. This amount varies with the duration of distillation, and is much greater than 50 per cent. if the operation is conducted slowly; it is proposed to carry out further experiments on the conditions of this change in the near future.

Ethyl γ-Cyano-α-benzyl-β-methylcrotonate,
$CN\cdot CH\colon CMe\cdot C(CH_2Ph)CO_2Et$ (or $CN\cdot CH_2\cdot CMe\colon C(CH_2Ph)CO_2Et$).

This ester is formed during the conversion of the cyanodicarboxylic ester into its sodium salt, and can be isolated by the same method as that described for the similar compounds mentioned in this paper. It is a fairly viscid liquid, which boils at 198°/18 mm.:

0·1965 gave 0·5314 CO_2 and 0·1256 H_2O. C = 73·74; H = 7·1.

$C_{15}H_{17}O_2N$ requires C = 74·1; H = 7·0 per cent.

Further experiments with this ester, and a description of the products formed from it on hydrolysis, will be given in a future communication.

The Formation of Benzylacetone, $CH_2Ph\cdot CH_2\cdot COMe$, *and Cyanoacetic Acid from the Enol-modification of Ethyl α-Cyano-γ-benzyl-β-methylglutaconate.*

The ease with which the enolic forms of the highly substituted derivatives of glutaconic ester undergo fission through the agency of alkali is well illustrated by this experiment. When the clear alkaline solution, obtained by extracting the enolic modification with 10 per cent. aqueous potassium hydroxide, is warmed to 40°, an oil quickly separates, and can be extracted by ether. It boils at 234°/756 mm. (Found, C = 80·69; H = 8·2. $C_{10}H_{12}O$ requires C = 81·0; H = 8·1 per cent.)

The semicarbazone, prepared in the usual manner, forms long, slender needles from alcohol and melts at 144° (Klages, *Ber.*, 1904, **37**, 2313, gives 142°). (Found, C = 64·48; H = 7·41. Calc., C = 64·4; H = 7·3 per cent.)

The liquid is therefore benzylacetone.

The mother liquor from the extracted oil, which was still yellow, yielded some unchanged enol-ester when acidified. This was extracted by ether, the aqueous residue evaporated to dryness, and the dried solid rubbed with ether. The ethereal extract on evaporation yielded cyanoacetic acid, melting at 65—66°. (Found, C = 42·21; H = 3·57. Calc., C = 42·4; H = 3·5 per cent.)

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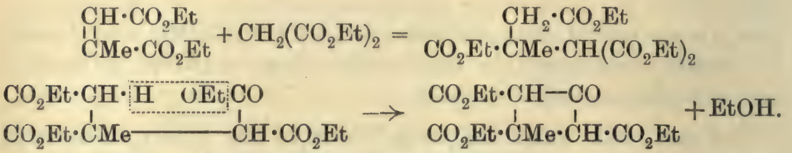
CXII.—*The Condensation of Ethyl Sodiomalonate with Ethyl Citraconate and the Synthesis of β-Methyltricarballylic Acid.*

By Edward Hope.

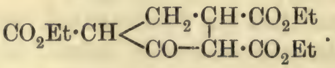
During the course of his investigations on the addition of ethyl sodioacetoacetate and ethyl sodiomalonate to unsaturated esters, Michael (*J. pr. Chem.*, 1887, [ii], **35**, 354; 1891, [ii], **43**, 395 (with Freer); 1892, [ii], **45**, 57 (with Schulthess); 1894, [ii], **49**, 20; *Ber.*, 1900, **33**, 3757) studied the condensation of ethyl citraconate with ethyl sodiomalonate in alcoholic solution, and obtained a substance, $C_{14}H_{20}O_7$, which he stated was ethyl 1-methyl*cyclo*butan-3-one-1 : 2 : 4-tricarboxylate, formed according to the scheme:



$$\begin{array}{l}\mathrm{CH{\cdot}CO_2Et}\\ \|\\ \mathrm{CMe{\cdot}CO_2Et}\end{array} + \mathrm{CH_2(CO_2Et)_2} = \begin{array}{c}\mathrm{CH_2{\cdot}CO_2Et}\\ |\\ \mathrm{CO_2Et{\cdot}CMe{\cdot}CH(CO_2Et)_2}\end{array}$$

$$\begin{array}{l}\mathrm{CO_2Et{\cdot}CH{\cdot}}\boxed{\mathrm{H\quad OEt}}\mathrm{CO}\\ \quad | \qquad\qquad\qquad\quad |\\ \mathrm{CO_2Et{\cdot}CMe}\text{———}\mathrm{CH{\cdot}CO_2Et}\end{array} \longrightarrow \begin{array}{l}\mathrm{CO_2Et{\cdot}CH{-}CO}\\ \quad | \qquad\quad |\\ \mathrm{CO_2Et{\cdot}CMe{\cdot}CH{\cdot}CO_2Et}\end{array} + \mathrm{EtOH}.$$

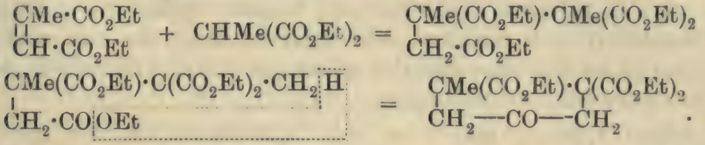
In view of the very limited number of methods available for synthesising *cyclo*butane compounds, the present work was undertaken (compare Proc., 1911, **27**, 281) in order to see how far the method described by Michael was capable of extension. The result of the investigation of the simplest case described by Michael—the condensation of ethyl citraconate with ethyl sodiomalonate in alcoholic solution—showed that this investigator was mistaken in his conclusions, and that the cyclic substance produced in this reaction is not a methyl *cyclo*butanone derivative, but a *cyclo*pentanone derivative, namely, ethyl *cyclo*pentan-2-one-1 : 3 : 4-tricarboxylate:



$$\mathrm{CO_2Et{\cdot}CH}\Big\langle\begin{array}{l}\mathrm{CH_2{\cdot}CH{\cdot}CO_2Et}\\ \qquad\ \ |\\ \mathrm{CO{-}CH{\cdot}CO_2Et}\end{array}.$$

This is proved by the fact that when this ester is hydrolysed, *cyclo*pentanone-4-carboxylic acid (m. p. 62—64°) is formed, the identity of this acid being established by comparison with the *cyclo*pentanone-4-carboxylic acid described by Kay and Perkin (Trans., 1906, **89**, 1646).

The first suggestion of the formation of a *cyclo*pentane compound in a reaction similar to the above, would appear to emanate from Svoboda (*Monatsh.*, 1902, **23**, 842), who condensed the sodium derivative of ethyl *iso*succinate with ethyl citraconate, and stated that the reaction proceeded as follows:



$$\begin{array}{l}CMe\cdot CO_2Et\\ \| \\ CH\cdot CO_2Et\end{array} + CHMe(CO_2Et)_2 = \begin{array}{l}CMe(CO_2Et)\cdot CMe(CO_2Et)_2\\ | \\ CH_2\cdot CO_2Et\end{array}$$

$$\begin{array}{l}CMe(CO_2Et)\cdot C(CO_2Et)_2\cdot CH_2|H\\ | \\ CH_2\cdot CO|OEt\end{array} = \begin{array}{l}CMe(CO_2Et)\cdot C(CO_2Et)_2\\ |\qquad\qquad\qquad | \\ CH_2 - CO - CH_2\end{array} .$$

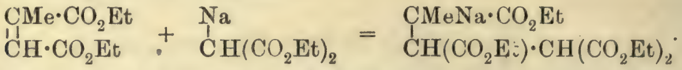
No rigid proof was adduced to show that the substance formed was a *cyclo*pentane derivative, and, moreover, the reaction is represented as proceeding by the elimination of alcohol from a carbethoxyl group and a methyl group—obviously an improbable assumption.

The same reaction had been carried out by Michael (*Ber.*, 1900, **33**, 3756), a fact overlooked by Svoboda, and Michael in pointing this out (*Ber.*, 1903, **36**, 576) again stated that in this case also a *cyclo*butane derivative is produced. No further investigations of reactions of this kind seem to have been carried out. In attempting to elucidate the mechanism of a reaction like the above, as large a variety of conditions as possible must necessarily be employed, and, although the variations so far used by the present author are comparatively few, yet they are sufficient to offer an explanation of the production of *cyclo*pentane compounds in this type of reaction. Among the conditions which were varied, the most important were the solvent employed and the temperature. It became apparent at an early stage in the work that the whole of the previous investigations on the condensation of ethyl citraconate with sodium compounds would have to be repeated, and, incidentally, it has been found necessary carefully to examine the corresponding condensations with ethyl mesaconate and ethyl itaconate.

The condensation of ethyl citraconate with the sodium compound of ethyl malonate in ethereal solution has been already described by Michael and Schulthess (*J. pr. Chem.*, 1892, [ii], **45**, 57) and by Michael (*Ber.*, 1900, **33**, 3759). It has always been assumed, and never proved, that the reaction proceeds in agreement with Michael's positive-negative rule (*J. pr. Chem.*, 1888, [ii], **37**, 522; 1899, [ii], **60**, 286, 409), according to which ethyl β-methylpropane-$\alpha\alpha\beta\gamma$-tetracarboxylate should be formed thus:

$$CO_2Et\cdot CMe\colon CH\cdot CO_2Et + CH_2(CO_2Et)_2 = CH(CO_2Et)_2\cdot CMe(CO_2Et)\cdot CH_2\cdot CO_2Et.$$

On hydrolysing the ester actually produced with hydrochloric acid, Michael obtained an acid melting at 168—173°. This he assumed to be β-methyltricarballylic acid, identical with, but somewhat purer than, the acid melting at 164° prepared by Auwers, Köbner, and v. Meyenburg (*Ber.*, 1891, **24**, 2893). The present author finds that ethyl citraconate condenses with ethyl sodiomalonate in solvents like ether and benzene (which do not react with sodium) in a manner quite different from that assumed by Michael to be the case, and the substance actually formed is ethyl butane-$\alpha\alpha\beta\gamma$-tetracarboxylate:



$$\begin{array}{l}\mathrm{CMe{\cdot}CO_2Et}\\ \|\\ \mathrm{CH{\cdot}CO_2Et}\end{array} + \begin{array}{l}\mathrm{Na}\\ |\\ \mathrm{CH(CO_2Et)_2}\end{array} = \begin{array}{l}\mathrm{CMeNa{\cdot}CO_2Et}\\ |\\ \mathrm{CH(CO_2Et){\cdot}CH(CO_2Et)_2}\end{array}.$$

The proof of this is that, on hydrolysing the tetrabasic ester thus formed, a practically quantitative yield of the isomeric α-methyltricarballylic acids (m. p. 185° and 139—142°) was obtained. The identity of these acids was fully established by direct comparison with the α-methyltricarballylic acids prepared by other methods. There is no reason to suppose that, in the above condensation, two reactions had gone on side by side leading, in the one case, to the formation of ethyl butane-$\alpha\alpha\beta\gamma$-tetracarboxylate, and in the other, to ethyl β-methylpropane-$\alpha\alpha\beta\gamma$-tetracarboxylate, for the hydrolysis of the latter with hydrochloric acid would have given β-methyltricarballylic acid, an acid which, as was proved by subsequent synthesis, is easily isolated.

As a matter of fact, no trace of β-methyltricarballylic acid could be isolated from the product of the hydrolysis of the condensation product. It is clear therefore that the acid (m. p. 168—173°) described by Michael (and, without doubt, also that of Auwers, Köbner, and v. Meyenburg) cannot have been β-methyltricarballylic acid, and it was doubtless impure α-methyltricarballylic acid.

The question as to why the reaction between ethyl citraconate and ethyl sodiomalonate takes a course exactly opposed to that which was to be expected from a consideration of the views held by Michael (*loc. cit.*) is one of some interest. Michael assumes that, owing to the presence of the methyl group, the carbon atom (+) in ethyl citraconate,

$$\mathrm{CH_3{\cdot}\underset{+}{C}(CO_2Et){:}\underset{-}{C}H{\cdot}CO_2Et},$$

is more positive in character than the carbon atom (−), and consequently the negative portion of the ethyl sodiomalonate, $-\mathrm{CH(CO_2Et)_2}$, should add itself to the carbon (+). As a matter of fact, the addition actually takes place at the carbon (−). In the opinion of the present author, there appears to be little use in discussing, for the present, at all events, any general theory of additive reactions of this kind, because it seems probable that the predominating factor in condensations of this type is that of steric influence. That there is almost always great resistance to the formation of a quaternary carbon atom (that is, a carbon atom the four valencies of which are engaged by four other carbon atoms) is a well-known fact, and this resistance is the greater the larger the molecular magnitude of the groups involved. Thus, for example, it has not been found possible to condense ethyl teraconate, $CMe_2{:}C(CO_2Et)\cdot CH_2\cdot CO_2Et$, and ethyl diphenylitaconate,

$$CPh_2{:}C(CO_2Et)\cdot CH_2\cdot CO_2Et,$$

with the sodium derivative of ethyl malonate, the reason evidently being that quaternary compounds such as

$$CH(CO_2Et)_2\cdot CMe_2\cdot CH(CO_2Et)\cdot CH_2\cdot CO_2Et$$

would have to result. From this point of view, there is nothing surprising in the addition of ethyl citraconate to ethyl sodiomalonate leading to the formation of ethyl butane-*ααβγ*-tetracarboxylate.

The condensation of ethyl sodiomalonate with ethyl citraconate in alcoholic solution is a reaction of great complexity. It was therefore considered advisable first to investigate the behaviour of these substances when mixed in cold alcoholic solution, and avoiding any elevation of temperature as far as possible. In this way, it was found possible to isolate, in good yield, an ester boiling at 207—209°/15 mm., which, on hydrolysis, gave at once, in an almost pure condition, butane-*αβδ*-tricarboxylic acid (m. p. 122°). The ester must therefore be ethyl butane-*αβδδ*-tetracarboxylate, $CO_2Et\cdot CH_2\cdot CH(CO_2Et)\cdot CH_2\cdot CH(CO_2Et)_2$. This ester is doubtless the intermediate product in the formation of ethyl *cyclo*pentan-2-one-1 : 3 : 4-tricarboxylate from ethyl citraconate and ethyl sodiomalonate, and the mechanism of this ring formation is probably as follows.

In a series of papers (Trans., 1881, **39**, 348; 1885, **47**, 865; 1893, **63**, 229; 1895, **67**, 960) Purdie and his co-workers have shown that alkyloxysuccinic esters are produced by the action of sodium alkyloxides on ethyl fumarate; thus ethyl fumarate reacts with sodium ethoxide in alcoholic solution to form ethyl ethoxysuccinate,

$$CO_2Et\cdot CH{:}CH\cdot CO_2Et + NaOEt = CO_2Et\cdot CHNa\cdot CH(OEt)\cdot CO_2Et.$$

Using the same conditions, the chief feature of which is the employment of 1/25th of an atom of sodium for each molecule of unsaturated ester, the present author has prepared from ethyl citraconate, ethyl methoxy- and ethoxy-methylsuccinates (boiling points 113—116°/13 mm. and 133—137°/15 mm. respectively), and from these by the action of alcoholic potassium hydroxide, methoxy- and ethoxy-methylsuccinic acids (m. p. 90—92° and 83—85° respectively). These substances and others similar to them are still under investigation, but their ready formation from ethyl citraconate by means of traces of sodium alkyloxides offers a clue to the production of ethyl butane-$\alpha\beta\delta\delta$-tetracarboxylate from this ester by condensation with ethyl sodiomalonate. Traces of sodium ethoxide may, of course, always be assumed to be present in an alcoholic solution of ethyl sodiomalonate, and these small quantities are without doubt sufficient to transform the ethyl citraconate into ethyl ethoxymethylsuccinate. The latter substance has, in all probability, the constitution $CO_2Et{\cdot}CMe(OEt){\cdot}CH_2{\cdot}CO_2Et$, and it may, in certain circumstances, lose the elements of alcohol in such a way that ethyl itaconate, $CH_2{:}C(CO_2Et){\cdot}CH_2{\cdot}CO_2Et$, is produced. If, now, the latter is assumed to condense with ethyl sodiomalonate in the normal manner (avoiding temperature elevation), ethyl butane-$\alpha\beta\delta\delta$-tetracarboxylate results:

$$CH_2{:}C(CO_2Et){\cdot}CH_2{\cdot}CO_2Et + CHNa(CO_2Et)_2 = \\ CNa(CO_2Et)_2{\cdot}CH_2{\cdot}CH(CO_2Et){\cdot}CH_2{\cdot}CO_2Et.$$

Strong evidence in favour of the above explanation is to be found in the fact that ethyl itaconate may be substituted for ethyl citraconate in this condensation without the slightest effect on the ultimate result.

The process of ring-formation from ethyl butane-$\alpha\beta\delta\delta$-tetracarboxylate may possibly be explained thus, but at the same time the mechanism is by no means clear. When ethyl citraconate or ethyl itaconate react with the sodium derivative of ethyl malonate in cold alcoholic solution, the sodium compound,

$$CNa(CO_2Et)_2{\cdot}CH_2{\cdot}CH(CO_2Et){\cdot}CH_2{\cdot}CO_2Et,$$

results. This sodium compound is produced by the action of ethyl itaconate on ethyl sodiomalonate in benzene solution, and also by the interaction of metallic sodium and ethyl butane-$\alpha\beta\delta\delta$-tetracarboxylate. That the same sodium compound is produced in all these ways is proved by the action of methyl iodide. In all four cases the same ester (b. p. 205—208°/14 mm.) is obtained, and when this is hydrolysed with hydrochloric acid it gives, in each case, pentane-$\alpha\beta\delta$-tricarboxylic acid (m. p. 157—158°),

$$CH_3{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CO_2H.$$

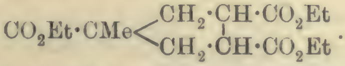
This acid was identical with the pentane-$\alpha\beta\delta$-tricarboxylic acid of that melting point described by Hope and Perkin (Trans., 1911, **99**, 773), who prepared it by condensing ethyl methylacrylate with the sodium compound of ethyl cyanoacetate, and then treating the sodium compound thus formed with ethyl bromoacetate. This reaction was represented by them as proceeding in the following stages:

$$CO_2Et{\cdot}CMe{:}CH_2 + CHNa(CN){\cdot}CO_2Et \longrightarrow \\ CO_2Et{\cdot}CHMe{\cdot}CH_2{\cdot}CNa(CN){\cdot}CO_2Et \longrightarrow \\ CO_2Et{\cdot}CHMe{\cdot}CH_2{\cdot}C(CN)(CO_2Et){\cdot}CH_2{\cdot}CO_2Et \xrightarrow{\text{hydrolysis.}} \\ CO_2H{\cdot}CHMe{\cdot}CH_2{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CO_2H.$$

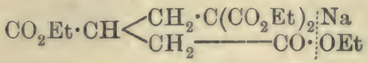
Although this is the most probable course of the reaction, still there are other possibilities, so that it was desirable to obtain more conclusive evidence for the above constitution. This has been done by condensing ethyl itaconate with the sodium derivative of ethyl *iso*succinate in ethereal solution. The reaction proceeds in the following manner:

$$CH_2{:}C(CO_2Et)\cdot CH_2\cdot CO_2Et + CMeNa(CO_2Et)_2 \longrightarrow CMe(CO_2Et)_2\cdot CH_2\cdot CNa(CO_2Et)\cdot CH_2\cdot CO_2Et.$$

The ethyl pentane-αβδδ-tetracarboxylate thus formed boils at 204—208°/14 mm., and on hydrolysis gives pentane-αβδ-tricarboxylic acid (m. p. 157—158°) identical with the acid obtained by the five methods just described. The yield of ethyl pentane-αβδδ-tetracarboxylate in the above experiment is far from good, but this does not affect the value of the proof of the constitution of pentane-αβδ-tricarboxylic acid, since the explanation of the small yield is that ethyl 1-methyl*cyclo*pentan-2-one-1 : 3 : 4-tricarboxylate * (b. p. 190—195°/14 mm.) is the main product of the reaction,†



The sodium atom in ethyl sodiobutane-αβδδ-tetracarboxylate (as produced in alcoholic solution from ethyl citraconate and ethyl sodiomalonate) is therefore proved to occupy the δ-position, but it is very doubtful if it remains in that position during ring-formation, and it is the opinion of the author that ring-formation occurs through the sodium first occupying the α-position. It is not asserted that the δ-sodio-compound is transformed completely into the α-sodio-compound, but rather that small amounts of the α-compound are successively formed from the large amount of the δ-compound, and, as soon as formed, are converted into the cyclic substance. The reasons for this opinion are as follows: (1) The elimination of sodium ethoxide from the δ-sodio-compound in the manner represented thus:



$$CO_2Et\cdot CH\begin{cases} CH_2\cdot C(CO_2Et)_2 \vdots Na \\ CH_2 \text{———} CO\cdot \vdots OEt \end{cases}$$

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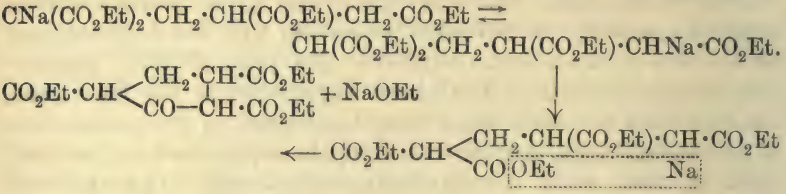
* This ester is, without doubt, identical with the so-called ethyl dimethyl*cyclo*butanonetricarboxylate of Michael (*Ber.*, 1900, **33**, 3756), and also the ethyl 1-methyl*cyclo*pentan-3-one-1 : 5 : 5-tricarboxylate of Svoboda (*Monatsh.*, 1902, **23**, 846), prepared, in both cases, by the action of ethyl citraconate on ethyl sodio*iso*succinate in hot alcoholic solution. The explanation of the formation of a *cyclo*pentane derivative in this case is, no doubt, the same as that advanced in the present communication to account for the production of ethyl *cyclo*pentanonetricarboxylate from ethyl citraconate and ethyl sodiomalonate.

† The remarkable ease with which a *cyclo*pentane derivative is formed in this reaction makes it important to investigate analogous cases, and it is the author's intention to extend his work in this direction.

is exceedingly improbable, because the resulting substance does not contain a hydrogen atom replaceable by sodium. (2) The striking ease with which ethyl itaconate and ethyl sodio*iso*succinate yield a *cyclo*pentanone derivative (p. 908) is further evidence in support of the point, because the condensation product,

$$CMe(CO_2Et)_2\cdot CH_2\cdot CH(CO_2Et)\cdot CH_2\cdot CO_2Et,$$

cannot have the sodium atom in the δ-position. Returning now to the process of ring-formation from ethyl sodiobutane-*αβδδ*-tetracarboxylate, it is probable that this must be represented thus:



$$CNa(CO_2Et)_2\cdot CH_2\cdot CH(CO_2Et)\cdot CH_2\cdot CO_2Et \rightleftarrows CH(CO_2Et)_2\cdot CH_2\cdot CH(CO_2Et)\cdot CHNa\cdot CO_2Et.$$

$$\downarrow$$

$$CO_2Et\cdot CH{<}\begin{matrix}CH_2\cdot CH\cdot CO_2Et\\ CO-CH\cdot CO_2Et\end{matrix} + NaOEt \longleftarrow CO_2Et\cdot CH{<}\begin{matrix}CH_2\cdot CH(CO_2Et)\cdot CH\cdot CO_2Et\\ CO\,\boxed{OEt \quad Na}\end{matrix}$$

the latter ester forming a mono- and probably to some extent a di-sodium compound.

Although the above scheme, in conjunction with that on p. 895, probably represents the main course of the reaction between ethyl citraconate and ethyl sodiomalonate in alcoholic solution, other changes occur, the nature of which is difficult to understand, and will form the subject of future investigation.

A series of experiments with ethyl mesaconate in the place of ethyl citraconate revealed the remarkable fact that this ester does not react with sodium ethoxide to form an ethoxy-derivative. Consequently ethyl mesaconate reacts normally with the sodium derivative of ethyl malonate, yielding ethyl butane-*ααβγ*-tetracarboxylate whether the reaction is carried out in alcoholic solution (hot or cold) or in neutral solvents like benzene, the proof of this being that hydrolysis of the ester produced by any of these methods gives only a mixture of the isomeric *α*-methyltricarballylic acids. This behaviour suggests a possible explanation of the fact that Auwers, Köbner, and v. Meyenburg obtained an acid melting at 164° (doubtless impure *α*-methyltricarballylic acid) as a result of condensing ethyl citraconate with ethyl sodiomalonate in alcoholic solution. If, as seems probable, the ethyl citraconate employed by them was prepared through the ammonium salt and the silver salt, the citraconic acid may have been partly converted into mesaconic acid (a change well known to occur in alkaline solution), and the ethyl citraconate may therefore possibly have been largely contaminated with ethyl mesaconate.

Synthesis of β-Methyltricarballylic Acid, $CO_2H\cdot CH_2\cdot CMe(CO_2H)\cdot CH_2\cdot CO_2H$.

For the purpose of this investigation (compare p. 894) it was necessary to find a method for the preparation of β-methyltricarballylic acid (which does not appear to have been previously made), and after a number of unsuccessful attempts had been made, it was finally obtained by the hydrolysis of the ester produced when potassium cyanide reacts with ethyl α-cyano-β-methylglutaconate, $CO_2Et\cdot CH(CN)\cdot CMe\colon CH\cdot CO_2Et$.

This reaction was first applied to the synthesis of polybasic acids by Bredt and Kallen (*Annalen*, 1896, **293**, 338), who investigated the addition of potassium cyanide and hydrocyanic acid (in aqueous alcoholic solution) to esters of the type $R\cdot CH\colon C(CO_2Et)_2$; thus, ethyl benzylidenemalonate and potassium cyanide yield ethyl β-cyano-β-phenylpropionate:

$$CHPh\colon C(CO_2Et)_2 + KCN + 2H_2O = CN\cdot CHPh\cdot CH_2\cdot CO_2Et + KHCO_3 + EtOH.$$

The present author has not, as yet, fully investigated the mechanism of the addition in the case of ethyl α-cyano-β-methylglutaconate, but purposes doing so both in this case and in the cases of other derivatives of glutaconic acid. Potassium cyanide appears to unite normally with ethyl cyanomethylglutaconate in absolute alcoholic solution, and the product, on hydrolysis with sulphuric acid, gives a moderate yield of β-methyltricarballylic acid, which, when purified through the triethyl ester (boiling point 163—164°/15 mm.), melts, after crystallisation from hydrochloric acid, at 165—166°. It will be observed that the melting point is remarkably near to that (164°) given by Auwers, Köbner, and v. Meyenburg for the so-called β-methyltricarballylic acid prepared by them, but their method of preparation cannot possibly have led to the formation of β-methyltricarballylic acid (compare p. 894).

β-Methyltricarballylic acid is scarcely distinguishable from the α-methyltricarballylic acids in its general properties. It exhibits the same behaviour towards solvents, and a neutral solution of its ammonium salt gives precipitates with the same reagents. When heated under low pressures, it loses water, forming an anhydro-acid, which distils undecomposed at 220—224°/15 mm. This crystallises exceedingly well from ethyl acetate, and melts at 139—140°. On treatment with water, it regenerates the tribasic acid (m. p. 165—166°).

EXPERIMENTAL.

Condensation of Ethyl Sodiomalonate with Ethyl Citraconate in Ether and Benzene.

Formation of Ethyl Butane-ααβγ-tetracarboxylate, $CH(CO_2Et)_2{\cdot}CH(CO_2Et){\cdot}CHMe{\cdot}CO_2Et$.

The ethyl citraconate used in all the experiments described in this paper was prepared in the following way. Citraconic anhydride (Kahlbaum) was dissolved in six times its weight of absolute alcohol, to which had been added one-tenth of its volume of concentrated sulphuric acid. The solution was immediately heated for about ten minutes on a steam-bath, and allowed to remain overnight. After gently heating for half an hour next day on the steam-bath, water was added, and the ester extracted in the usual way. The ethereal solution requires careful washing with sodium carbonate, and it is advisable to use dilute alkali to remove traces of unchanged anhydride. The ester was thus obtained in a yield of about 80 per cent. of that theoretically possible. It boiled constantly at 116—117°/15 mm., also at 120°/20 mm. Its specific gravity at 16·5° was 1·046, compared with water at the same temperature.

When mixed with alcoholic potassium hydroxide in the cold, some considerable heat was generated (the temperature rising to 32°), and it was converted quantitatively into the potassium salt of mesaconic acid, which, on acidifying, gave mesaconic acid, melting at 202°.

The condensation with ethyl sodiomalonate was carried out in the following manner. 5·9 Grams of sodium were melted under boiling toluene and shaken vigorously until in the form of a coarse powder. The toluene was poured off, and the sodium washed with dry ether. Then a solution of 43 grams of ethyl malonate in 200 c.c. of dry ether was poured on the sodium, and the sodium compound allowed to form for about five hours; 48 grams of ethyl citraconate were then added, and the mixture was gently heated for about five hours. At the end of that time the white sodium compound had entirely disappeared, and water was added. The ethereal layer contained the whole of the reaction-product, the sodium compound of which is readily decomposed by water. On evaporating the ether, a viscid oil remained, which distilled completely at 208°/22 mm. and 198°/14 mm.

The yield was 65 grams, or about 72 per cent. of that theoretically possible.

On acidifying the alkaline, aqueous layer, a small amount of an oil was precipitated and extracted, but the amount was so small that it was not further investigated.

If benzene is employed instead of ether in this reaction, the same behaviour is observed throughout. Further, the course of the reaction is the same whether heated at the temperature of the steam-bath or allowed to remain at the ordinary temperature.

Butane-aaβγ-tetracarboxylic Acid, $C_8H_{10}O_8$.—When the above ester is treated with alcoholic potassium hydroxide, it is readily hydrolysed, and a small quantity of a sparingly soluble potassium salt separates. On adding water, evaporating off the methyl alcohol, and acidifying the aqueous solution, an acid is set free, which can be readily extracted with pure ether. On evaporating the solvent, the acid crystallises, and can be purified by recrystallisation from a mixture of ethyl acetate and chloroform. After two crystallisations, the melting point remained constant at 154—156° (with effervescence). (Found, C=41·1; H=4·6. Calc., C=41·0; H=4·3 per cent.)

There is little doubt that two isomeric acids are produced in this reaction, for although the ester which was hydrolysed was of constant boiling point, an acid of constant melting point could only be obtained by an exceedingly wasteful crystallisation.

Hydrolysis of Ethyl Butane-aaβγ-tetracarboxylate with Hydrochloric Acid. The Isomeric a-Methyltricarballylic Acids, $C_7H_{10}O_6$.

Twenty grams of the pure ester were boiled with 150 c.c. of concentrated hydrochloric acid during eight hours. The homogeneous, slightly yellow liquid thus formed was evaporated to small bulk, and set aside in an ice-chest to crystallise. After several hours, the acid had crystallised to a solid, white mass. This first crop of crystals was collected, dried, and weighed. The weight was 3·6 grams, and the melting point 159—165°. Recrystallisation from dilute hydrochloric acid raised the melting point to 185—186°. Further recrystallisation from the same solvent or from organic solvents did not raise the melting point. (Found, C=44·3; H=5·5. Calc., C=44·2; H=5·3 per cent.)

The acid was evidently *a*-methyltricarballylic acid. It was compared directly with *a*-methyltricarballylic acid prepared according to Bone and Sprankling (Trans., 1902, **81**, 39), and also with a specimen obtained by condensing ethyl fumarate with ethyl sodio*iso*succinate. The melting point was not changed by admixture with these acids; moreover, the same characteristic crystals (hexagonal plates) were observed under the microscope when any of the above acids were crystallised from dilute hydrochloric acid.

The aqueous filtrate from the acid, melting at 159—165°, was evaporated gradually over sulphuric acid in an exhausted desiccator, four further fractions of acid being thus obtained. The first of these fractions weighed 4·5 grams, and melted at 142—145°. Frequent crystaliisation from water did not appreciably alter the melting point:

0·1427 gave 0·2324 CO_2 and 0·0687 H_2O. C=44·4; H=5·3.
$C_7H_{10}O_6$ requires C=44·2; H=5·3 per cent.

The other fractions all consisted of the variety of α-methyltricarballylic acid of low melting point, and weighed in all 1 gram. The total yield of crystalline acid from 20 grams of pure ester was therefore 9·1 grams, or 83 per cent. of the theoretical.

The purest specimens of maleinoid α-methyltricarballylic acid melted at 139—142°. On mixing with a specimen of this acid prepared by the action of ethyl fumarate on ethyl sodio*iso*succinate, the melting point was unaltered. The difficulty of obtaining a satisfactory melting point is probably to be attributed to a conversion of minute amounts into the isomeride of higher melting point.

Ethyl α-methyltricarballylate (which does not appear to have been previously described) is readily prepared by esterifying the crude acid, as obtained in the previous experiment, by means of alcohol and sulphuric acid. It is a colourless oil, practically odourless, and boils constantly at 180—181°/24 mm. When hydrolysed by means of alcoholic potassium hydroxide, a mixture of the potassium salts of fumaroid and maleinoid α-methyltricarballylic acids is formed.

Action of Sodium and Methyl Iodide on Ethyl Butane-αβγγ-tetracarboxylate. Formation of Ethyl Pentane-βγδδ-tetracarboxylate.

When finely divided metallic sodium (0·77 gram) is allowed to act on ethyl butane-αβγγ-tetracarboxylate (24 grams) in ethereal solution, the latter readily forms a sodium compound which remains dissolved. If excess of methyl iodide is now added, and the mixture gently boiled for one hour, on adding water and extracting, a good yield (20 grams) of a new substance is obtained, which boils constantly at 196°/15 mm.

This ester, on hydrolysis with hydrochloric acid, gives a complex mixture of acids from which one was isolated melting at 202°. This acid crystallised magnificently from dilute hydrochloric acid, and was without doubt the αα′-dimethyltricarballylic acid described by Zelinsky and Tschernoswitoff (*Ber.*, 1896, **29**, 617). The mixture of acids obtained in the above experiment probably also contains one of the other two isomeric *aa′*-dimethyltricarballylic acids described by the same authors.

It is of interest to note that when ethyl citraconate is condensed with ethyl sodiomalonate in ethereal solution and methyl iodide added directly to the mixture, a vigorous reaction occurs, but, on hydrolysing the resulting ester (which boils at 194—196°/13 mm.), only the isomeric *a*-methyltricarballylic acids could be isolated.

Condensation of Ethyl Citraconate with Ethyl Sodiomalonate in Alcoholic Solution at the Ordinary Temperature.

Formation of Ethyl Butane-aβδδ-tetracarboxylate,

$CO_2Et{\cdot}CH_2{\cdot}CH(CO_2Et){\cdot}CH_2{\cdot}CH(CO_2Et)_2$.

This reaction was carried out at follows: 5·85 Grams of sodium were dissolved in 150 c.c. of absolute alcohol, 42 grams of ethyl malonate then added, and the solution was cooled to the ordinary temperature. After the separation of the solid sodium derivative, 48 grams of ethyl citraconate were added all at once, and the temperature prevented from rising (as it will do if the reaction is left to itself for about twenty minutes) by cooling under the tap. Next day the cloudy alcoholic solution was poured into water. A colourless oil separated, and was extracted with ether. After drying the ethereal solution, the solvent was distilled off, and the residual ester distilled under diminished pressure. It boiled at 207—209°/13 mm., and was produced in about 50 per cent. yield. This ester gave no coloration in alcoholic solution with ferric chloride, and when hydrolysed with hydrochloric acid gave butane-*aβδ*-tricarboxylic acid, $C_7H_{10}O_6$, melting at 122°. (Found, $C = 44{\cdot}1$; $H = 5{\cdot}4$. Calc., $C = 44{\cdot}2$; $H = 5{\cdot}3$ per cent.)

The acid was compared directly with a specimen of butane-*aβδ*-tricarboxylic acid prepared by condensing ethyl itaconate with ethyl sodiomalonate in ethereal solution. The ethyl butane-*aβδδ*-tetracarboxylate obtained in this way, in 85 per cent. yield, boiled constantly at 209—211°/15 mm., and on hydrolysis gave butane-*aβδ*-tricarboxylic acid, melting at 122°.

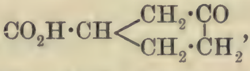
The aqueous solution into which the alcoholic solution was originally poured deposits an oil when acidified. For the sake of brevity, this oil will be referred to as "acid" oil. The "acid" oil, the sodium compound of which is presumably soluble in water without being decomposed, increases in amount (while the neutral oil decreases correspondingly) when the temperature of the reaction is raised. In the above case the "acid" oil is only produced in about one-fifth the quantity of the neutral oil. If the reaction is carried out at the temperature of the water-bath, the quantity of "acid" oil increases to about five times the quantity of the neutral oil.

Action of Ethyl Citraconate on Ethyl Sodiomalonate in Hot Alcoholic Solution. Formation of Ethyl cyclo*Pentan-2-one-1:3:4-tricarboxylate.*

The relative amounts of substances used in these experiments were exactly those described in the last section, where the reaction was conducted at the ordinary temperature. The only difference was that, in the present case, the temperature employed was that of a steam-bath, the duration of each experiment being four hours. In examining the products of the reaction, the following process was adopted. The alcoholic solution was poured into water, and the oil extracted with ether. This oil was ethyl butane-$\alpha\beta\delta\delta$-tetracarboxylate (b. p. 214—216°/20 mm.), which is produced by the series of reactions already indicated. The fact that this small amount of an open-chain compound remains is no doubt attributable to the fact that the cyclic ester produced as the main product of this reaction can form a disodium derivative, thereby fixing a part of the sodium which would otherwise cause ring-formation.

After the removal of the neutral oil, carbon dioxide was passed through the aqueous solution for a long period until no further precipitation of oil took place. This oil having been extracted, the aqueous solution was finally treated with hydrochloric acid and again extracted.

The Oil Precipitated by Carbon Dioxide.—This substance gave an intense purple coloration with ferric chloride in alcoholic solution, and could be distilled under diminished pressure, although with considerable decomposition (195—200°/11 mm.). Without doubt this ester is identical with the tribasic ester of boiling point 217—219°/20 mm. described by Michael (*Ber.*, 1900, **33**, 3758). No subsequent attempt was made to distil the ester in quantity, the crude oil from the carbon dioxide being hydrolysed directly with 8 per cent. sulphuric acid. The hydrolysis was very rapid, and was complete at the end of two and a-half hours, after which the acid solution was saturated with ammonium sulphate and extracted six times with ether. After removing the ether and distilling under diminished pressure, a fraction passed over constantly at 172—174°/16 mm., and solidified in the receiver. An equal amount of an acid remained in the distillation flask, and showed no sign of distilling even at much higher temperatures. The distilled acid melted at 50—55°, but on recrystallisation from light petroleum the melting point rose to 62—64°. This acid was compared directly with a specimen of the *cyclo*pentanone-4-carboxylic acid,



$$CO_2H\cdot CH\Big<\begin{matrix}CH_2\cdot CO\\ \quad\ \ |\\ CH_2\cdot CH_2\end{matrix},$$

described by Kay and Perkin (Trans., 1906, **89**, 1641), whose method of synthesis leaves no doubt as to its constitution, and the formula receives further corroboration from the subsequent work of Haworth and Perkin (Trans., 1908, **93**, 573).

An intimate mixture of the acid prepared in the above experiment with Kay and Perkin's acid melted at 61—63°. The oximes of the two specimens were prepared by allowing to remain overnight, a mixture of the acid, hydroxylamine hydrochloride, and potassium hydroxide in aqueous solution. The oximes in both cases were extracted with much ether, in which they are sparingly soluble. Both the specimens melted, after recrystallisation from ether, at 177—179°. The oxime, $C_6H_9O_3N$, of the acid prepared from ethyl citraconate was analysed. (Found, $N=10{\cdot}0$. Calc., $N=9{\cdot}8$ per cent.)

The semicarbazones of the same acids were prepared, and both found to melt at 197—198°, decomposing at that temperature.*

The Oil Precipitated by Hydrochloric Acid.—This oil, obtained by the addition of hydrochloric acid to the alkaline liquid into which carbon dioxide had previously been passed, was found to decompose vigorously when heated even at very low pressure. No attempt was therefore made to distil it, and it was hydrolysed at once with 8 per cent. sulphuric acid. The acid thus produced was extracted many times with ether, and then esterified by means of alcohol and sulphuric acid. The resulting ester was a complex mixture, and on distillation gave an ill-defined fraction, boiling between 110° and 140°/13 mm. (which probably contained a quantity of ethyl *cyclo*pentanone-4-carboxylate), and later, a constant fraction at 235—242°/13 mm. The latter ester was also obtained by esterifying the residue in the flask from the distillation of the *cyclo*pentanonecarboxylic acid (p. 904):

0·1244 gave 0·2614 CO_2 and 0·0808 H_2O. $C=57{\cdot}3$; $H=7{\cdot}2$.
0·1164 „ 0·2467 CO_2 „ 0·0714 H_2O. $C=57{\cdot}8$; $H=6{\cdot}8$.

The above analyses were carried out with material from two different preparations.

When boiled with methyl-alcoholic potassium hydroxide, solution of the ester takes place, with the immediate production of a deep brown colour, and in a few moments a viscous, brown potassium salt separated. After twelve hours, water was added, and the whole of the alcohol evaporated. After extracting the alkaline solution with pure ether, the liquid was acidified and extracted many times with pure ether. On evaporating the ether, a viscid acid remained, which was boiled with water, and filtered. The solution was evaporated on the steam-bath, and the residue set aside in an ice-chest. After about a week, crystallisation took place. The crystals were pressed on porous porcelain, and recrystallised from hydrochloric acid. The acid then melted at 103—106°, but the quantity was so small that no further purification could be attempted, nor could any derivatives be made:

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* Michael gives 192—193° as the melting point of the semicarbazone of his cyclic acid. He does not appear to have prepared the oxime. The melting point of the acid itself is given as 62—64° (*Ber.*, 1900, **33**, 3758).

0·1475 gave 0·2555 CO_2 and 0·0737 H_2O. C=47·2; H=5·5.

0·1662 required for neutralisation 25·53 c.c. *N*/10-NaOH (0·1022 gram of NaOH).

As already stated (p. 896), ethyl itaconate may be substituted for ethyl citraconate in the experiments just described without materially affecting the result. Both ethyl *cyclo*pentanonetricarboxylate and also the unidentified by-products are formed in the same relative quantities.

Ethyl *cyclo*pentan-2-one-1:3:4-tricarboxylate is also produced in good yield when molecular quantities of sodium ethoxide and ethyl butane-αβδδ-tetracarboxylate are heated for five hours in alcoholic solution. In this case the formation of the above-mentioned by-products is almost entirely avoided.

Action of Sodium Ethoxide on Ethyl Citraconate in Alcoholic Solution. Formation of Ethyl Ethoxymethylsuccinate.

Twenty-five grams of ethyl citraconate were mixed with a solution of 0·2 gram of sodium in 120 c.c. of absolute alcohol (distilled from calcium). The mixture became yellow, and was left overnight at the ordinary temperature. It was then poured into water, and the precipitated ester extracted with ether. On distilling under diminished pressure, practically the whole quantity passed over at 133—137°/15 mm., and on re-distillation the fraction 132—134°/14 mm. was collected:

0·1240 gave 0·2564 CO_2 and 0·0955 H_2O. C=56·4; H=8·5.

$C_{11}H_{20}O_5$ requires C=56·9; H=8·6 per cent.

Ethyl ethoxymethylsuccinate is readily hydrolysed by alcoholic potassium hydroxide, yielding a crystalline potassium salt, sparingly soluble in methyl alcohol. After adding water, evaporating free from methyl alcohol, and acidifying, the acid was extracted with pure ether, and the ethereal solution evaporated. The residue was dissolved in water, boiled for five minutes, filtered, and evaporated to small bulk, but the acid crystallised with difficulty from the aqueous solution, and melted at 78—82°. It was recrystallised from a mixture of ether and light petroleum, the melting point being thereby raised to 81—83°:

0·0905 gave 0·1578 CO_2 and 0·0563 H_2O. C=47·5; H=6·9.

$C_7H_{12}O_5$ requires C=47·7; H=6·8 per cent.

When the ester is heated in a sealed tube with concentrated hydrochloric acid for five hours at 140°, much ethyl chloride is produced, together with a considerable amount of mesaconic acid (m. p. 202°).

A similar series of substances is produced when methyl alcohol is substituted for ethyl alcohol in the above experiment. *Ethyl α-methoxy-α-methylsuccinate* boils at 113—116°/13 mm., and on hydrolysis with methyl-alcoholic potassium hydroxide yields α-methoxy-α-methylsuccinic acid, which melts at 90—92°.

The behaviour of ethyl itaconate and ethyl mesaconate under similar conditions is being investigated.

Action of Methyl Iodide on the Sodium Derivative of Ethyl Butane-αβδδ-tetracarboxylate. Formation of Ethyl Pentane-αβδδ-tetracarboxylate,

$CMe(CO_2Et)_2{\cdot}CH_2{\cdot}CH(CO_2Et){\cdot}CH_2{\cdot}CO_2Et$.

When ethyl citraconate (or ethyl itaconate) reacts with ethyl sodiomalonate in alcoholic solution at the ordinary temperature (compare p. 903), the sodium compound of the condensation product remains dissolved in the alcohol, and when this is boiled for half an hour with methyl iodide, an excellent yield of an ester boiling at 202—207°/13 mm. is obtained. On boiling with hydrochloric acid, this ester is readily hydrolysed, giving a mixture of acids, one of which, pentane-αβδ-tricarboxylic acid (m. p. 157—158°),

$CO_2H{\cdot}CHMe{\cdot}CH_2{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CO_2H$,

is readily isolated on account of its sparing solubility in hydrochloric acid. The other acid present, which was not isolated in a pure condition, is without doubt the *cis*-modification of the same pentanetricarboxylic acid. The acid melting at 157—158° was proved to be identical with that melting at the same temperature, prepared by Hope and Perkin (Trans., 1911, **99**, 773) in the manner referred to on p. 896. Ethyl pentane-αβδδ-tetracarboxylate (which, of course, yields the acid of melting point 157—158° on hydrolysis) is also produced in almost quantitative yield by the two following methods:

(1) Ethyl itaconate is condensed with ethyl sodiomalonate in ethereal solution, and the resulting clear solution of the sodium

compound of the condensation product boiled for half an hour with methyl iodide. The resulting ester boiled constantly at 207°/15 mm.

(2) Ethyl butane-$\alpha\beta\delta\delta$-tetracarboxylate is treated with finely divided sodium in ethereal solution. The solution of the sodium compound thus produced is boiled with methyl iodide, as in the previous experiment. The resulting ester boiled at 205°/14 mm. In all cases, the identity of the esters was proved by hydrolysis with hydrochloric acid.

The constitution of the above pentanetricarboxylic acid was finally determined by condensing ethyl itaconate with ethyl sodio-*iso*succinate in ethereal solution. The reaction was carried out as follows. Finely divided sodium (2·9 grams) was suspended in ether, and ethyl *iso*succinate (22 grams) added. The sodium compound was produced with great vigour, the reaction being complete in about ten minutes. Ethyl itaconate (23·5 grams) was then added, in small quantities at a time, and the mixture allowed to remain for three hours at the ordinary temperature. On adding water, a portion of the reaction-product passed into solution in the ether. After washing the ethereal solution with water and dilute potassium hydroxide, the solvent was distilled off, and the residual oil fractionated under diminished pressure. The only constant fraction was one which passed over at 203—207°/16 mm. A quantity of some substance of higher boiling point remained in the distillation flask, and showed signs of decomposition on further heating. The ester boiling at 203—207°/16 mm. was without doubt the normal additive product of ethyl itaconate and ethyl *iso*succinate. On hydrolysis with hydrochloric acid, it gave an acid melting at 157—158° identical with the acid of that melting point prepared by the several methods just described.

The main product of the reaction between ethyl itaconate and ethyl sodio*iso*succinate remained dissolved in the aqueous layer when water was added to the reaction mixture. On acidifying the red-coloured aqueous solution with acetic acid and extracting with ether, a considerable amount of an oil was obtained, which gave an intense red coloration with ferric chloride. It distilled fairly constantly at 190—195°/15 mm., but after a short time signs of decomposition showed themselves. A residue of very high boiling point remained in the flask.

In a further experiment, using the conditions just described, no attempt was made to distil the ester after liberation by means of acetic acid, but it was immediately hydrolysed with 8 per cent. sulphuric acid. The acid formed in the hydrolysis was extracted several times with ether, and distilled under diminished pressure.

Almost the whole quantity passed over at 172—175°/16 mm. This acid was 1-methyl*cyclo*pentan-2-one-4-carboxylic acid, identical with that prepared by Hope and Perkin (Trans., 1911, **99**, 774). It gave an oxime, which melted and decomposed at 176—177°. Its ethyl ester boiled at 126—127°/20 mm., and gave a semicarbazone melting at 137—139°.

Condensation of Ethyl Mesaconate with Ethyl Sodiomalonate in Alcoholic Solution. Formation of Ethyl Butane-αβγγ-tetracarboxylate.

This condensation was carried out, both at the ordinary temperature and at the temperature of the steam-bath, exactly as described in the experiments with ethyl citraconate (pp. 903 and 904). Under both conditions a 60—70 per cent. yield of ethyl butane-αβγγ-tetracarboxylate, boiling at 198—202°/14 mm., was produced. Hydrolysis of the ester gave a mixture of the fumaroid and maleinoid forms of α-methyltricarballylic acid, the latter preponderating in quantity. No trace of any cyclic substance could be found in the products of these reactions.

In benzene solution, ethyl mesaconate behaves towards ethyl sodiomalonate exactly as does ethyl citraconate. A 75 per cent. yield of ethyl butane-αβγγ-tetracarboxylate is produced. Hydrolysis of the condensation product with hydrochloric acid gave a mixture of the isomeric α-methyltricarballylic acids, which were separated by fractional crystallisation from water.

Synthesis of β-Methyltricarballylic Acid.

Ethyl α-cyano-β-methylglutaconate was prepared as described by Rogerson and Thorpe (Trans., 1905, **87**, 1669), by the action of ethyl acetoacetate on the sodium derivative of ethyl cyanoacetate. The product thus obtained (20 grams) was heated gently on the water-bath with finely powdered potassium cyanide (12 grams) and absolute alcohol (70 c.c.) for about twelve hours. At the end of that time the deep brown solution was poured into water, and, as no oil was precipitated, the whole was acidified and extracted with ether. The ester thus obtained was hydrolysed by boiling with 40 per cent. sulphuric acid, and the resulting acid was extracted several times with ether. After distilling off the ether, the residue was esterified by contact for three days with alcoholic sulphuric acid (20 c.c. of acid in 100 c.c. of absolute alcohol). On pouring into water and extracting with ether, about 8 grams of an oil were obtained, which boiled constantly at 163—164°/15 mm.:

0·1152 gave 0·2382 CO_2 and 0·0816 H_2O. C=56·4; H=7·8.

$C_{13}H_{22}O_6$ requires C=56·9; H=8·0 per cent.

The smallness of the yield is doubtless largely assignable to the difficulty of extracting polybasic acids of this kind with ether and of esterifying them in the way described.

When this ester (6 grams) was boiled for one hour with an alcoholic solution of potassium hydroxide (11 grams), hydrolysis took place readily. After adding water and evaporating off the alcohol, the alkaline solution was extracted with ether, then acidified, and again extracted several times with pure ether. After evaporation of the ether an acid remained in an almost pure condition, and readily solidified. It was purified by boiling with water, and filtering the solution. On cooling the filtrate, the acid was deposited, and melted at 162—164°. After another crystallisation from hydrochloric acid, the melting point rose to 165—166°, and was not altered on recrystallisation:

0·1529 gave 0·2506 CO_2 and 0·0747 H_2O. C=44·7; H=5·4.
$C_7H_{10}O_6$ requires C=44·2; H=5·3 per cent.

0·1382 Gram required for neutralisation 0·0871 gram NaOH, whereas a tribasic acid of the above formula should require 0·0874 gram.

β-Methyltricarballylic acid is exactly similar to the isomeric α-methyl derivative in almost all its properties. A neutral solution of the ammonium salt gives a white, crystalline precipitate with solutions of silver nitrate, mercuric chloride, and lead acetate; a green precipitate with copper acetate; a white, gelatinous precipitate with cerium nitrate; and a brown, gelatinous precipitate with ferric chloride. It gives no precipitate with barium, calcium, magnesium, and manganese salts.

β-Methyltricarballylic acid is insoluble in light petroleum, benzene, or chloroform, and fairly readily soluble in ethyl acetate, acetone, acetic acid, or formic acid. It crystallises well from formic acid, aqueous hydrochloric acid, and from a mixture of acetone and benzene.

When heated strongly under low pressure, β-methyltricarballylic acid loses water, forming the *anhydro-acid*, and the latter distils at 220—223°/15 mm. At first a viscous liquid, the anhydro-acid, soon solidifies, and can be readily crystallised from ethyl acetate, from which it separates in short, rectangular prisms melting at 139—140°.

The anhydro-acid is practically insoluble in light petroleum or benzene, sparingly soluble in chloroform (from which it readily crystallises), and readily so in ethyl acetate, acetone, or ether. When boiled with water and the solution allowed to cool, β-methyltricarballylic acid separates (m. p. 165—166°). When an ethereal solution of anhydro-β-methyltricarballylic acid is mixed with an ethereal solution of *o*-toluidine (calculated amount), combination takes place, but the resulting *o*-toluidide is a gum. If α-naphthylamine is used instead of *o*-toluidine, the resulting compound is more crystalline, and separates from the ethereal solution, on keeping overnight, as a pure white crust melting at 98—100°. As it was found impossible to effect any purification by recrystallising the product, it was analysed in its original condition:

0·1295 gave 5·6 c.c. N_2 at 13° and 732 mm. N = 4·9.
$C_{17}H_{15}O_4N$ requires N = 4·7 per cent.

0·1076 gram required for neutralisation 0·024 gram NaOH, whereas a dibasic anhydride of the above formula requires 0·029 gram NaOH.

β-Methyltricarballylic acid, prepared by the method just described, is identical in all respects with the acid prepared by an exceedingly convenient method suggested to the author by Dr. R. Robinson. Twenty-six grams of potassium cyanide, 26 grams of ethyl acetoacetate, 23 grams of ethyl cyanoacetate, and 100 c.c. of absolute alcohol are placed in a flask fitted with an air condenser, and maintained at the temperature of the water-bath for twelve hours, the whole being shaken up from time to time. The mixture turns dark brown very rapidly, and, if allowed to remain at the ordinary temperature after the heating is finished, sets to a solid mass, which probably consists largely of a potassium compound of ethyl βγ-dicyano-β-methylpropane-αγ-dicarboxylate,

$$CO_2Et\cdot CH(CN)\cdot CMe(CN)\cdot CH_2\cdot CO_2Et.$$

The yield of condensation products (for there is more than one formed in the reaction) is about 55—60 per cent. of that theoretically possible. The procedure adopted to obtain pure β-methyltricarballylic acid was that already described (p. 909).

If the condensation is effected in a somewhat different manner from that just described, and only 1 molecule of potassium cyanide (instead of two in the experiment above) used, for each molecule of ethyl cyanoacetate, then, on pouring into water at the end of the reaction, instead of obtaining a clear solution, an oil is precipitated which distils at 180—200°/13 mm. On redistillation the fraction 200—205°/20 mm. was collected, and found to consist of *ethyl βγ-dicyano-β-methylpropane-αγ-dicarboxylate*:

0·1350 gave 13·2 c.c. N_2 at 14° and 750 mm. N = 11·3.
$C_{12}H_{16}O_4N_2$ requires N = 11·1 per cent.

The crude oil obtained in this experiment contained other substances, and their nature will be investigated when the author applies the methods described in this paper to the synthesis of other substituted tricarballylic acids.

In conclusion, the author desires to express his indebtedness to Prof. W. H. Perkin for the interest which he has taken in this work.

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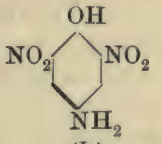
XCIII.—*Quinone-Ammonium Derivatives. Part I. The Methylation Products of Picramic and* iso*Picramic Acids.*

By RAPHAEL MELDOLA and WILLIAM FRANCIS HOLLELY.

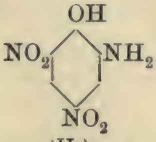
IN a note published by one of the authors in 1910 (Proc., **26**, 232), a trimethyl*iso*picramic acid was described as resulting from the methylation of *iso*picramic acid by methyl sulphate in the presence of alkali. The analysis of this compound, taken in connexion with its non-phenolic character, appeared to indicate that both the hydroxyl and amino-groups had been methylated, and that 2 : 6-dinitrodimethyl-*p*-anisidine, at that time unknown, had been obtained, and the corresponding formula was provisionally assigned. In view of the remarkable properties of the compound, and especially its high melting point and bright colour, its study was continued with the object of getting further evidence concerning its constitution. The compound in question melts above 300°, is non-phenolic, and basic in character; it separates from the alkaline liquor after completion of the methylation in bright red needles, crystallising from boiling water on cooling, and dissolving in dilute mineral acids to a colourless solution from which the original red compound is precipitated by alkali. The air-dried red compound loses water on drying at 100°, and changes from bright red to an ochreous colour. According to the constitution at first assigned, the compound might be expected to result from the methylation of the 2 : 6-dinitro-*p*-anisidine (m. p. 212°), described in a former communication to the Society (Meldola and Stephens, Trans., 1905, **87**, 1204). Some of this compound was therefore methylated by methyl sulphate in presence of alkali in the usual way, but the product was quite different from that formerly obtained by the methylation of *iso*picramic acid by the same method. Whilst the research was in progress we learnt from a private communication from Dr. F.

Reverdin, of Geneva, that a compound isomeric with the original substance of high melting point obtained from *iso*picramic acid had been obtained by him by methylating the above dinitroanisidine with methyl sulphate in methyl-alcoholic solution. An interchange of specimens led to the conclusion that the new isomeride obtained from the dinitroanisidine by Reverdin's method was the true dinitrodimethyl-*p*-anisidine. It appeared also that when the dinitroanisidine is methylated by methyl sulphate in presence of alkali some dinitromonomethyl-*p*-anisidine is also formed, the product consisting of a mixture of the mono- and di-methyl derivatives of 2 : 6-dinitro-*p*-anisidine. The new dinitrodimethyl-*p*-anisidine has been since described by Reverdin and de Luc (*J. pr. Chem.*, 1911, [ii], **84**, 555).

From the foregoing results it follows that *iso*picramic acid and its methyl ether give totally different products when methylated by methyl sulphate in presence of alkali. The methylation of *iso*picramic acid was originally studied in our laboratory with the object of preparing compounds containing an asymmetric quinquevalent nitrogen atom combined with at least one radicle of a sufficiently acid character to confer acid properties upon the whole molecule of the ammonium derivative. The hydroxyl group is so well protected in this dinitroaminophenol (I) that it was anticipated



(I.)

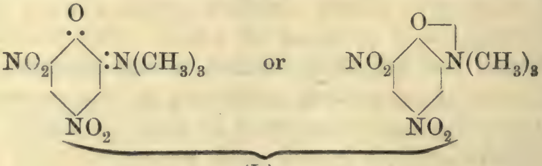


(II.)

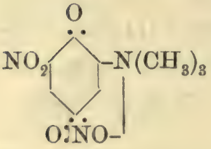
that any process of alkylation would, through steric hindrance, result in alkylation in the amino-group only. That the product of extreme methylation is a trimethyl derivative has been confirmed by numerous analyses of the original compound and its derivatives. It is shown in the present paper that the anticipated concentration of the process of substitution on the amino-group has been verified to an extent quite beyond any preconceived possibility, since all three methyl groups are shown to be attached to the nitrogen atom of the original amino-group. This conclusion having been established, it appeared probable that picramic acid (II) might give an analogous compound, since the hydroxyl is in this case also partly protected by the 6-nitro-group. This anticipation has also been verified experimentally, although the yield of trimethyl derivative is not so good as with *iso*picramic acid, for the obvious reason that in the latter the amino-group is quite unprotected, whilst in picramic acid it is partly protected by the hydroxyl group. Picramic acid on methylation by the method described gives, in fact, a mixture of mono-, di-, and tri-methyl derivatives; *iso*picramic acid, on the other hand, gives only the trimethyl derivative in practically quantitative yield.

Constitution of the Trimethyl Derivatives.

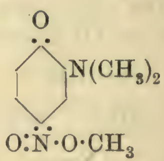
The mono- and di-methyl derivatives of picramic and *iso*picramic acids described in the experimental part of this paper are of the ordinary type of alkylated amines, and require no special consideration. In the trimethyl derivatives there is no methoxy-group present, as shown by the fact that dinitroanisidine yields a different compound when methylated. Three possible formulæ thus remain for consideration. In the case of picramic acid the formulæ are:



(I.)

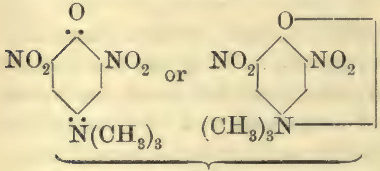


(II.)

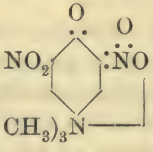


(III.)

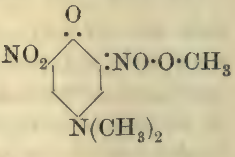
In the case of *iso*picramic acid the corresponding formulæ are:



(IV.)



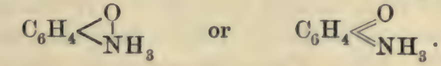
(V.)



(VI.)

Of these, formulæ III and VI are excluded for several reasons. In the first place, if these compounds were methyl ethers of the type of Hantzsch's *iso*nitro(*aci*)-compounds, they might be expected to be unstable and to lose one methyl group with readiness. This is not the case; the compounds are, in fact, extremely stable, and can only be demethylated by heating with concentrated hydriodic acid, as in the Zeisel process (see experimental part). In the next place, formulæ I and II or III and IV represent these compounds as derivatives of the hydroxyphenyltrimethylammonium bases which were first prepared by Griess (*Ber.*, 1880, **13**, 246; also

Auwers and Wehr, *Annalen*, 1904, **334**, 308). That this view is correct is proved by the fact that we have prepared our compounds by the direct nitration of Griess's bases or their salts. It may be taken as proved, therefore, that the extreme methylation of picramic and *iso*picramic acids gives rise to compounds in which all three methyl groups are attached to one nitrogen atom. These compounds may accordingly be regarded as derivatives of the hypothetical quinone-ammonium,



$$C_6H_4<\begin{array}{l}O\\|\\NH_3\end{array} \quad \text{or} \quad C_6H_4\ll\begin{array}{l}O\\NH_3\end{array}.$$

Griess adopted the first (betaine) formula for the anhydrides of his trimethylated aminophenols. This author describes also a compound resulting from the methylation of nitroaminophenol by his method, which evidently belongs to the same series, and is, in fact, the mononitro-derivative corresponding with our product from picramic acid (*Ber.*, 1880, **13**, 647). This compound is also non-phenolic; it crystallises in yellow needles, and melts and decomposes above 200°.

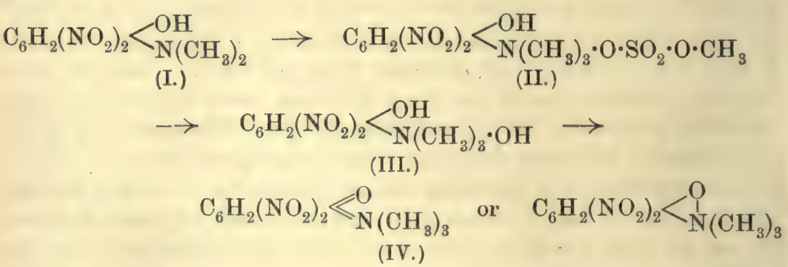
In the case of the unsubstituted parent compounds, no question of constitution arises beyond the general question of cross-linking (betaine) as against ketonoid structure. The introduction of the nitro-groups in our compounds complicates matters by introducing the possibility of *iso*nitro(ketonoid)-structure, in which case the compounds would be inner salts with meta-cross linking (formulæ II and V). On the alternative view they are simply nitro-derivatives of the parent trimethylquinone-ammonium compounds (formulæ I and IV). The decision between these alternative formulæ must for the present remain on open question until further evidence has been obtained. It is considered by many chemists with whom this question has been discussed that the ketonoid structure (I and IV) is improbable as assuming that a quinquevalent nitrogen atom can have all its bonds attached to carbon, a state of affairs believed to be without parallel. We may point out, however, that the conditions are quite peculiar in the compounds under consideration, inasmuch as the carbon atom which (on the ketonoid structural theory) is doubly linked to the nitrogen atom is part of a highly acidic ring system. It has already been indicated that on this view the compounds are analogous to the oxides of the tertiary amines, the quinonoid ring functioning as the oxygen atom (Meldola and Kuntzen, Trans., 1911, **99**, 2045):

$$O{:}NR_3 \qquad O{:}C_6H_4(NO_2)_2{:}N(CH_3)_3.$$

If this analogy holds good, it follows that quinone-ammonium derivatives in which three dissimilar radicles are attached to the quinquevalent nitrogen atom should, in accordance with the discovery of Meisenheimer (*Ber.*, 1908, **41**, 3966), be resolvable into optically active isomerides. Experiments having this object in view are now in progress in our laboratory. In connexion with the question of the presence of quinquevalent nitrogen doubly linked to carbon, it is of interest to recall the observations of Pope and Harvey (Trans., 1901, **79**, 85). These authors, in discussing the mechanism of the optical inversion of amino-compounds, give reasons for believing in the existence of unstable transition compounds of the type $(R_1R_2){:}C{:}NH_3$ (see also Pope and Read, Trans., 1909, **95**, 180). The substitution of the quinonoid ring for R_1 and R_2 and of alkyls for hydrogen would result in the conversion of the unstable hypothetical intermediate compounds required by the hypothesis of Pope and Harvey into stable derivatives on the assumption that the quinone-ammonium compounds have an analogous constitution.

Mechanism of the Methylation Process.

The first stages in the methylation of the picramic acids are quite normal, and have been proved to be ordinary substitutions leading to the formation of mono- and di-methylamino-compounds. The extreme stage is reached through the formation of an intermediate trimethylammonium compound followed by hydrolysis of the latter:



$$C_6H_2(NO_2)_2{<}\begin{array}{l}OH\\N(CH_3)_2\end{array} \longrightarrow C_6H_2(NO_2)_2{<}\begin{array}{l}OH\\N(CH_3)_3{\cdot}O{\cdot}SO_2{\cdot}O{\cdot}CH_3\end{array}$$

(I.) (II.)

$$\longrightarrow C_6H_2(NO_2)_2{<}\begin{array}{l}OH\\N(CH_3)_3{\cdot}OH\end{array} \longrightarrow$$

(III.)

$$C_6H_2(NO_2)_2{\lll}\begin{array}{l}O\\N(CH_3)_3\end{array} \quad \text{or} \quad C_6H_2(NO_2)_2{<}\begin{array}{l}O\\|\\N(CH_3)_3\end{array}$$

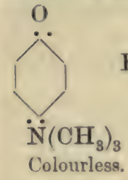
(IV.)

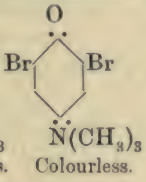
The ammonium hydroxide stage (III) is retained in the case of *iso*picramic acid, as will be seen from the experimental part. Picramic acid, on the other hand, passes at once to the anhydro-form, namely, the quinone-ammonium compound (IV). The difference in behaviour of the two isomerides is most simply explained by the recognised principle that anhydridisation takes place more readily between groups in the ortho-position, although, as is shown further on, there are good reasons for assigning a different structural formula to the hydrated product from *iso*picramic acid.

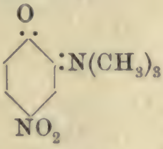
The Relationship between Colour and Chemical Constitution.

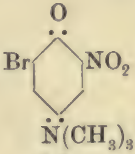
The compounds described in the present paper raise extremely important points in connexion with the general question of the relationship between colour and chemical constitution. We do not consider that there is at present sufficient evidence to warrant any dogmatic statement of conclusions reached since the constitution of our compounds, so far as concerns internal linking, is, as already stated, an open question. At this stage of the work we propose, therefore, offering only some general considerations indicating the directions in which this research bears upon the main question. The facts are: (1) the quinone-ammonium compounds are ochreous; (2) the ammonium hydroxide (hydrate) form of the compound from *iso*picramic acid is bright red; the corresponding compound from picramic acid does not exist; (3) the salts formed by the quinone-ammonium compounds with mineral acids are all colourless.

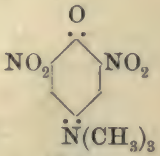
That the colour is due to the presence of the nitro-groups is proved by the fact that the parent (unsubstituted) compounds are colourless, and that the substitution of halogens for both nitro-groups also gives rise to colourless derivatives. The substitution of bromine or iodine for one of the nitro-groups gives a coloured quinone-ammonium compound, but not so highly coloured as when two nitro-groups are present. Adopting provisionally the simpler formulæ, and for the sake of simplicity taking one series only, these facts are summarised below:


Colourless.


Colourless.


Yellow.*


Ochreous.


Ochreous.

The appearance of colour in those compounds containing nitro-groups might, therefore, be interpreted as an indication of a difference in structure between these compounds and their unsubstituted or halogen containing representatives. As the only alternative formula is that in which an *iso*nitro-group with meta-cross linking is present, this argument, as far as it goes, is in favour of formulæ II and V discussed in connexion with the constitution of the trimethylated products. This view receives some support from the fact that the trimethyl derivatives from both picramic and *iso*picramic acids are of much the same colour.

Whichever view be adopted with respect to the constitution of the free quinone-ammonium compounds, there can be but little doubt that their salts are all of the normal type (I). These salts

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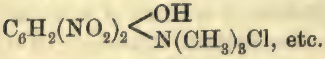
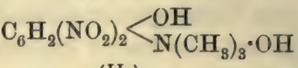
* This is Griess's compound referred to above, and, although belonging to the ortho-series, is included here for the sake of comparison.



$$\mathrm{C_6H_2(NO_2)_2}{<}\begin{matrix}\mathrm{OH}\\ \mathrm{N(CH_3)_3Cl}\end{matrix}\text{, etc.}$$

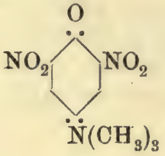
(I.)



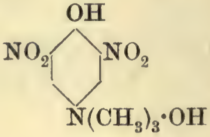
$$\mathrm{C_6H_2(NO_2)_2}{<}\begin{matrix}\mathrm{OH}\\ \mathrm{N(CH_3)_3{\cdot}OH}\end{matrix}$$

(II.)

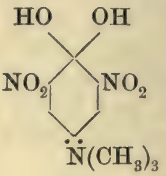
are colourless, and their formation takes place in accordance with the general process of reversion to the benzenoid type if the ketonoid structure be adopted, or to the rupture of cross linking if the betaine constitution is preferred. The corresponding ammonium hydroxide (hydrate) form might therefore be supposed to possess a similar constitution (II). Here, however, there arises a special difficulty due to the remarkable change of colour observed when the free bases are liberated from their salts by the action of alkali. The quinone-ammonium hydroxide from *iso*picramic acid is, as already stated, bright red; the corresponding bromonitro-derivative is orange-red. As these bases give colourless salts, it is fair to conclude that the free bases and their salts have different structures. This difference in structure is best explained by considering the effect of hydrating the quinone-ammonium compound:



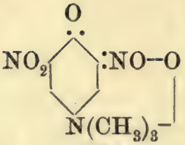
(I.)



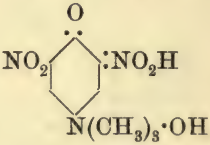
(II.)



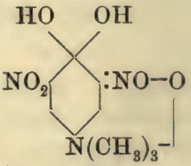
(III.)



(IV.)

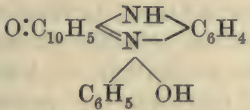


(V.)



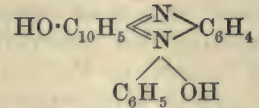
(VI.)

If formula I is taken, the hydrate may have either formula II or III. Formula II represents the base as having the same constitution as the salts, a view which is improbable in view of the striking difference in colour. If formula IV is ascribed to the quinone-ammonium compound, then the addition of water may lead to V or VI, of which V may be rejected as improbable, since a compound of that structure might be expected to be unstable, and to pass at once into II. There remain only III and VI as possible formulæ for the red base, and the decision between these is for the present left an open question. On either view the compound is represented as related to the "quinoles" and pseudobases; it is highly improbable that such a strongly coloured substance can have the simple ammonium hydroxide formula (II), all such compounds when coloured having also quinonoid or ketonoid structure in some part of the molecule. We may refer, for instance, to Kehrmann's oxy*iso*naphthaphenazonium hydroxide (*Ber.*, 1896, **29**, 2321), of which both tautomeric forms are coloured and in both of which quinonoid structure is present:



$$O{:}C_{10}H_5{<}\begin{matrix}NH\\ \underset{C_6H_5\quad OH}{N-}\end{matrix}{>}C_6H_4$$

Paraquinonoid form: red.



$$HO\cdot C_{10}H_5{<}\begin{matrix}N\\ \underset{C_6H_5\quad OH}{N}\end{matrix}{>}C_6H_4$$

Orthoquinonoid form: bluish-green.

As against the simpler formula (II) we may add that all attempts to prove the presence of hydroxyl by alkylation or acylation have led to negative results.* In favour of formula VI, which represents the base as an "inner salt" of an *iso*nitro(*aci*)-compound, the vivid colour may be appealed to, as Hantzsch and his colleagues have shown that the *aci*-ethers of nitrophenols are all highly coloured. Quinoles are, on the other hand, generally colourless, although, so far as we have been enabled to ascertain, no compounds of this class containing nitro-groups in the nucleus have as yet been prepared, and it is impossible to predict what influence upon the colour would be exerted by such groups. We hope to extend the research in this direction.

The existence of the red compound from *iso*picramic acid and the non-existence of an analogous hydrate from picramic acid are facts quite in harmony with the quinole (carbinol) structure proposed. Assuming the normal structure for the salts of trimethylated *iso*picramic acid, the first result of the substitution of hydroxyl for the acid radicle might be considered to be the normal ammonium hydroxide base (II). The latter would then isomerise by the transference of hydroxyl from the nitrogen to the para-carbon atom, with the production of III or VI. The passage from the unstable ammonium base into the stable carbinol or pseudo-base would, on this view, be analogous to the well known transformation of phenylacridium hydroxide into the carbinol or pseudo-base (Hantzsch and Kalb, *Ber.*, 1899, **32**, 3109). This view of the mechanism of the process is supported by the fact that when a colourless solution of the quinone-ammonium salt is made alkaline in the cold, the colour of the base is but slowly developed, and the red, crystalline compound only separates out completely after some time. If the hot solution of the salt is basified, the red colour of the base appears at once with full intensity.

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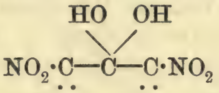
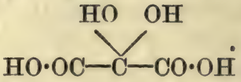
* This might also be attributed to the highly "protected" position of the hydroxyl group, but *iso*picramic acid, in which the hydroxyl group is equally protected, is distinctly phenolic and is readily acetylated with acetic anhydride in presence of a little sulphuric acid.

The objection to the quinole constitution based on the difficulty of admitting the union of two hydroxyl groups with one carbon atom must be given due weight, but in view of the special configuration of these compounds as shown in the proposed formulæ this difficulty is not really formidable. It is true that in no known compound of quinole structure hitherto obtained is there reason for believing that two hydroxyl groups are attached to the same carbon atom.* In the compounds from *iso*picramic acid and the corresponding bromonitroaminophenol, however, the para-carbon atom is in the exceptional position of being attached to two carbon atoms carrying strongly acid radicles (nitro-groups), and is therefore analogous to the middle carbon atom of mesoxalic acid †:

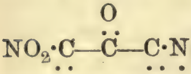


$$\mathrm{NO_2{\cdot}\underset{\cdot\cdot}{C}{-}\overset{HO\;\;OH}{\overset{\diagdown\diagup}{C}}{-}\underset{\cdot\cdot}{C}{\cdot}NO_2}$$



$$\mathrm{HO{\cdot}OC{-}\overset{HO\;\;OH}{\overset{\diagdown\diagup}{C}}{-}CO{\cdot}OH}$$

This condition is not realised in picramic acid, as one of the carbon atoms is attached to the basic trimethylammonium group,



$\mathrm{NO_2{\cdot}\underset{\cdot\cdot}{C}{-}\overset{O}{\overset{\cdot\cdot}{C}}{-}\underset{\cdot\cdot\cdot}{C}{\cdot}N(CH_3)_3}$. With this configuration the quinole structure with two hydroxyl groups attached to the middle carbon atom would be unstable, a view which is in accordance with the fact that the quinone-ammonium compound from picramic acid does not form a hydrate.‡

General Characters of the Quinone-ammonium Derivatives.

In ascribing a quinole structure to the hydrates of nitroquinone-ammonium compounds it is recognised that the proposed type differs fundamentally from that of the true quinoles in having the ternary ammonium group in the position occupied by the oxygen atom in the latter compounds. The stability of our compounds is in these circumstances certainly remarkable, since the quinole-imines which are formed as intermediate compounds in the preparation of quinoles by the method of Bamberger are extremely unstable, and readily exchange their imino-group for oxygen (*Ber.*, 1900, **33**, 3600). These considerations may perhaps be urged in favour of formula VI, in which the nitrogen of the ammonium group is singly, and not doubly, bound to the carbon of the quinonoid ring system. Experiments on the products of oxidation of the quinone-ammonium compounds have been undertaken for the purpose of throwing further light on this part of the subject, but the results are as yet inconclusive. Certain other characters which might be expected to be associated with quinole structure also require investigation, and have as yet only been studied in a preliminary way; thus the true quinoles have been shown to be capable of being benzoylated by the Schotten-Baumann method (Bamberger and Rising, *Ber.*, 1900, **33**, 3640; Bamberger and Brady, *ibid.*, 3650), whereas our compounds fail to yield benzoyl derivatives. This property is, however, readily explained by the proposed formula, since the benzoylation of one hydroxyl group would be immediately followed by hydrolysis and restoration to the original type:

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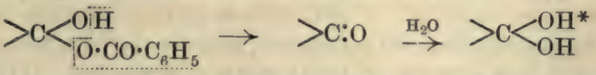
* This statement applies only to the dry solid; in aqueous solution, such compounds may exist. The unstable hydrate of dimethylquinole may possibly have two hydroxyls attached to the same carbon atom (Bamberger and Brady, *Ber.*, 1900, **33**, 3650).

† We are indebted to Dr. J. T. Hewitt for suggesting this analogy.

‡ There is a close analogy between our quinone-ammonium derivatives and the sulphonium compounds recently investigated by Zincke and Brune (*Ber.*, 1911, **44**, 185). In this case, also, in which quadrivalent sulphur occupies the position of the quinquevalent nitrogen of the quinone-ammonium compounds, the question of para-cross linking or ketonoid structure again arises, preference being given to the latter by the authors named. The parallelism extends likewise to colour, the thionium-quinone containing a bromine atom being colourless and the corresponding nitro-derivative yellow.



$$>\mathrm{C}<\begin{matrix}\mathrm{OH}\\ \mathrm{O\cdot CO\cdot C_6H_5}\end{matrix} \rightarrow\ >\mathrm{C{:}O} \xrightarrow{\mathrm{H_2O}}\ >\mathrm{C}<\begin{matrix}\mathrm{OH}^{*}\\ \mathrm{OH}\end{matrix}$$

The quinone-ammonium derivatives, also regarded as anhydrides of the quinoles and having a true quinonoid oxygen atom, might be expected to react with hydrazines; so far, however, no hydrazones have been obtained, but this part of the research has not yet been exhausted. It is most probable that this reaction is checked by the steric hindrance interposed by the protecting nitro-groups. The extreme readiness with which the quinone-ammonium compound from *iso*picramic acid hydrates and dehydrates we regard as giving further support to the view that the two hydroxyl groups are attached to the same carbon atom.

Relationship of the Quinone-ammonium Derivatives to the Iminazolium Compounds and Iminazolones.

Not the least important aspect of the present research is the relationship indicated by the above heading. The products obtained by the addition of alkyl iodides to the iminazoles, and described in a series of papers formerly communicated to and published by the Society, are, after the substitution of hydroxyl for the halogen atom, closely related to the quinone-ammonium derivatives. The investigation of the latter may therefore be expected to throw further light on the constitution of the former. This part of the subject is not yet ripe for full discussion, but in a general way the nature of the relationship will be seen from the following hypothetical schemes:

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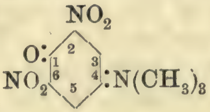
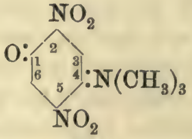
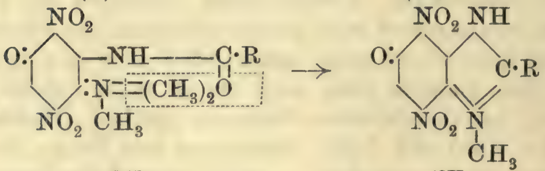
* This explanation applies also to the non-formation of an acetyl derivative of the quinone-imonium hydrate previously alluded to.



(I.)



(II.)



(III.) (IV.)

Taking the simpler formula (I) for the quinone-ammonium compound (the alternative ortho-quinonoid structure with meta-cross linking making no difference to the argument), the iminazolones may be regarded as derivatives of the unknown isomeride (II). Supposing that an acylamino-group could by some means be introduced into position 3, the resulting compound (III), by the elimination of the groups comprised within the dotted line, would give the iminazolone IV (written on the ketonoid type). This is, of course, a purely imaginary process, but it will serve to illustrate the nature of the relationship between the two series of compounds. There is, in fact, as will be seen on referring to the former papers, a distinct parallelism between the two series. Many (but not all) of the hydrates of the iminazolones are red; the iminazolones are generally, but not always, ochreous. The only question that now arises is, therefore, whether the red "hydrates" may not also have the carbinol (pseudo-base) structure. This is possible, but a difficulty is here introduced owing to the fact that some of the anhydro-forms, for example, that from aniline (Meldola and Kuntzen, Trans., 1911, **99**, 1291), are also red. Without pursuing this part of the subject further at present, we desire, in calling attention to the foregoing relationship, to indicate the direction in which the two lines of research are evidently converging.

EXPERIMENTAL.

Methylation of the Picramic Acids under Various Conditions.

Methylation by methyl sulphate was effected in the usual way by suspending the crystalline solid in water, adding a slight excess of the sulphate, and agitating briskly with occasional additions of sodium hydroxide solution, and then allowing the slightly alkaline solution to remain at atmospheric temperature for some hours. The insoluble quinone-ammonium compound which separates out is collected, washed with water, and purified if necessary by dissolving in hydrochloric acid, filtering the solution, and precipitating by alkali. In the case of *iso*picramic acid the alkaline filtrate on acidification gives only a small quantity of some resinous by-product, the main product being the quinone-ammonium compound formerly described. The alkaline filtrate from picramic acid on acidification gave an ochreous precipitate, which after being collected, washed, and dried, was separable by boiling alcohol into two compounds, one being left as an insoluble residue, and the other remaining in the alcoholic solution, from which it slowly separates in orange scales on dilution with water. The insoluble product proved to be *dimethylpicramic acid* (4:6-*dinitro*-2-*dimethylaminophenol*). The latter is a phenolic compound dissolving in aqueous alkali with an orange colour; it is but very sparingly soluble in boiling alcohol, but can be crystallised from hot glacial acetic acid, from which it separates on cooling as a yellow, microcrystalline powder melting at 218—220°:

0·1097 gave 0·1706 CO_2 and 0·0406 H_2O. C=42·41; H=4·12.
0·1062 ,, 16·9 c.c. N_2 (moist) at 18° and 762·4 mm. N=18·45.
$C_8H_9O_5N_3$ requires C=42·27; H=3·99; N=18·50 per cent.

The substance deposited from the alcoholic mother liquor on dilution was not isolated in a state of purity, but we have satisfied ourselves that it consists of a monomethyl derivative, mixed possibly with a little unmethylated picramic acid. The melting point of the product obtained after recrystallisation from alcohol was 144—145°. It was found on analysis to contain 19·31 per cent. of nitrogen, the formula for a monomethyl derivative requiring 19·72 per cent.

*iso*Picramic acid when methylated by methyl iodide and alkali in methyl-alcoholic solution or in water gave only resinous, indefinite products. When heated in a sealed tube with excess of methyl iodide at 100° for six to seven hours, the acid gave as the main product dimethyl*iso*picramic acid, which is described later. At a higher temperature (115—120° for three hours) the main product of methylation was the quinone-ammonium compound.

Methylation by methyl sulphate in the presence of ammonia instead of sodium hydroxide converts *iso*picramic acid into a mixture of the quinone-ammonium compound and the dimethyl derivative, the latter predominating.

Picramic acid when methylated by heating with excess of methyl sulphate at 100° for one hour gave a mixture of mono- and di-methyl derivatives; no quinone-ammonium compound is formed under these conditions. *iso*Picramic acid when acted on with methyl sulphate under various conditions gave the following results:

Methyl sulphate in methyl-alcoholic solution fails to methylate after several hours' heating on the water-bath. When dissolved in excess of impure methyl sulphate containing free methylsulphuric acid, *iso*picramic acid gives a mixture of mono- and di-methyl derivatives and no quinone-ammonium compound. The result in this case is the same, whether the solution in methyl sulphate is allowed to remain at the ordinary temperature for a short time or whether heated on the water-bath for some hours. When pure methyl sulphate is used and the solution kept at 100° for ten minutes, the products are the quinone-ammonium compound and the dimethyl derivative.

*Dimethyl*iso*picramic acid* (2:6-*dinitro*-4-*dimethylaminophenol*), obtained by the above processes, is both basic and phenolic in character; it dissolves in dilute mineral acids, giving colourless salts, and in dilute alkalis with a claret-red colour. The compound obtained by crystallisation from alcohol consists of dark purple needles with a coppery lustre fusing at 182—183°:

0·0962 gave 0·1492 CO_2 and 0·0338 H_2O. C=42·29; H=3·90.
0·0737 „ 12 c.c. N_2 (moist) at 16° and 743·2 mm. N=18·54.
$C_8H_9O_5N_3$ requires C=42·27; H=3·99; N=18·5 per cent.

The *acetyl* derivative, prepared by acetylating the dimethyl derivative with acetic anhydride in presence of sulphuric acid, crystallises from dilute acetic acid in flat, brown needles with serrated edges melting at 156—158°:

0·1260 gave 16·8 c.c. N_2 (moist) at 18·5° and 765·7 mm. N=15·47.
$C_{10}H_{11}O_6N_3$ requires N=15·61 per cent.

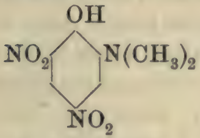
The *benzoyl* derivative, prepared by the Schotten-Baumann method, crystallises from alcohol in small, red scales, and from glacial acetic acid in red, fern-like clusters melting at 178—179°:

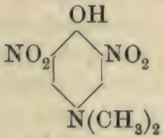
0·0884 gave 9·8 c.c. N_2 (moist) at 17·5° and 766·2 mm. N=12·93.
$C_{15}H_{13}O_6N_3$ requires N=12·69 per cent.

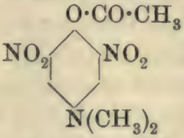
The monomethyl*iso*picramic acid contained in the alcoholic mother liquor from which the dimethyl derivative is crystallised has not been isolated in a state of purity, as it is mixed with some unmethylated *iso*picramic acid. The whole product on solution in hydrochloric acid and treatment with sodium nitrite gave a quinone-diazide crystallising from glacial acetic acid in ochreous scales or needles exploding sharply at about 190°. (Found, N = 26·40. $C_6H_2O_5N_4$ requires N = 26·67 per cent.)

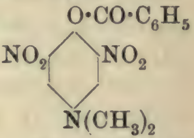
This quinone-diazide is evidently the same compound as that described in a former paper (Trans., 1905, **87**, 1204). On combining with β-naphthol in alkaline solution it gave an azo-compound, which was identified with that described in the paper referred to (*loc. cit.*, 1205).

All the products of methylation of *iso*picramic acid obtained by the foregoing methods give the quinone-ammonium compound on further methylation with methyl sulphate and alkali. The compounds described in this section are formulated below:


M. p. 218—220°.

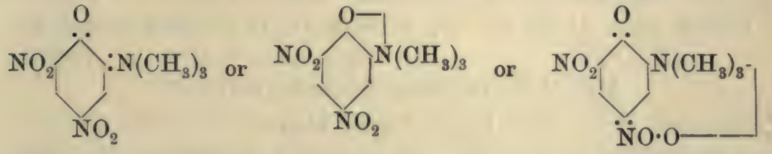

M. p. 182—183°.


M. p. 156—158°.


M. p. 178—179°.

The Quinone-ammonium Compounds.

4 : 6-*Dinitro-2-trimethylammonium*-1-*benzoquinone.*



The ochreous insoluble residue left on methylating picramic acid by methyl sulphate and alkali can be purified by dissolving in hydrochloric acid and precipitating by ammonia or by crystallisation from boiling water, from which it separates in ochreous needles having no definite melting point, but decomposing at 275—280°:

0·0933 gave 0·1530 CO_2 and 0·0402 H_2O. C = 44·72; H = 4·78.
0·0950 „ 0·1558 CO_2 „ 0·0418 H_2O. C = 44·72; H = 4·88.
0·0925 „ 13·85 c.c. N_2 (moist) at 18·5° and 766·6 mm. N = 17·41.

$C_9H_{11}O_5N_3$ requires C = 44·78; H = 4·60; N = 17·43 per cent.

The compound when allowed to dry in the air is anhydrous, and undergoes no loss at water-oven temperature. Attempts to acetylate and benzoylate the compound led to negative results. Although basic to the extent of dissolving in dilute mineral acids, the salts are easily dissociable, and cannot be isolated for analysis. A *platinichloride* which crystallises in pale, ochreous needles separates on mixing solutions of the chloride and platinic chloride. This salt also begins to dissociate on washing with water or alcohol, as shown by the analytical results. (Found, Pt = 19·8 and 18·9. $(C_9H_{12}O_5N_3Cl)_2PtCl_4$ requires Pt = 21·85 per cent.)

The demethylation of the compound has been effected under various conditions. A quantitative determination of the methyl groups eliminated by heating with hydriodic acid indicated that complete demethylation occurred. 0·1045 Gram was heated in a current of carbon dioxide with 15 c.c. of hydriodic acid (D 1·7) and 5 grams of ammonium iodide for two and a-half hours at 210°.

Found, AgI = 0·2965; Me = 18·2.

$C_9H_{11}O_5N_3 - 3Me$ requires a loss = 18·7 per cent.

Less complete demethylation was effected by heating the compound in a sealed tube with concentrated hydrochloric acid to 130° for two hours. On opening the tube, methyl chloride was evolved, and the acid solution, on dilution with water and on being made alkaline by sodium hydroxide, gave an orange-coloured solution from which only a trace of unchanged substance was removed by filtration. The alkaline filtrate, on acidification, gave a yellow precipitate, which, after being collected, washed, and crystallised from alcohol, was identified as dimethylpicramic acid (m. p. 218—220°):

0·0824 gave 13·05 c.c. N_2 (moist) at 14·5° and 748·5 mm. N = 18·29.

$C_8H_9O_5N_3$ requires N = 18·50 per cent.

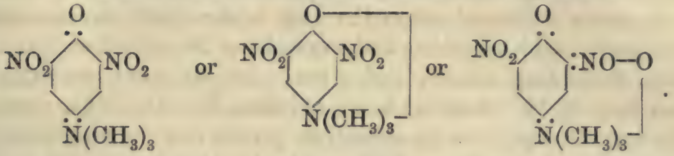
The alcoholic mother liquor from which the dimethyl derivative had separated gave, on dilution, a small quantity of the monomethyl derivative previously referred to, but this product was not further investigated. The main product of demethylation under the conditions specified is dimethylpicramic acid.

Synthesis from o-*Hydroxyphenyltrimethylammonium Hydroxide.*—o-Aminophenol was methylated in methyl-alcoholic solution by methyl iodide and potassium hydroxide, according to the method of Griess already referred to (*Ber.*, 1880, **13**, 246). The crystalline methiodide, after purification by crystallisation from water, was converted into the nitrate of the ammonium base by decomposition by means of silver nitrate. The solution of the nitrate, after filtration, was evaporated to dryness on the water-bath, and the dry crystalline residue dissolved in small portions in fuming nitric acid. After some hours the nitric acid solution was poured into water, and made alkaline with ammonia. The ochreous needles which separated proved to be identical with the product of methylation of picramic acid; decomposing point 275—280°:

0·1262 gave 18·9 c.c. N_2 (moist) at 17·5° and 763·5 mm. N = 17·42.

$C_9H_{11}O_5N_3$ requires N = 17·43 per cent.

2 : 6-*Dinitro*-4-*trimethylammonium*-1-*benzoquinone*.



The red, crystalline deposit which collects in the alkaline solution on methylating *iso*picramic acid by methyl sulphate and sodium hydroxide is the "hydrate" of the above quinone-ammonium compound, and most probably possesses the quinole structure previously assigned. The compound crystallises from hot water in long, bright, red needles, decomposing above 300°. An air-dried specimen gave the following results on analysis:

0·1062 gave 0·1630 CO_2 and 0·0512 H_2O. C=41·85; H= 5·35.
0·1128 „ 15·9 c.c. N_2 (moist) at 22·5° and 770·5 mm. N=16·15.
$C_9H_{13}O_6N_3$ requires C=41·67; H=5·05; N=16·22 per cent.

The constitution of this "hydrate" has already been discussed. The compound is quite stable at the ordinary atmospheric temperature, but loses its water readily in the water-oven:

0·7584 lost 0·0524 H_2O=6·90.
0·5855 „ 0·0408 H_2O=6·96.
$C_9H_{13}O_6N_3$ requires a loss=6·95 per cent.

The change of colour on drying is most striking, the bright red needles becoming of an ochreous yellow and disintegrating to a microcrystalline powder. The quinone-ammonium compound gave the following results on analysis:

0·0975 gave 0·1594 CO_2 and 0·0412 H_2O. C=44·58; H=4·69.
0·0970 „ 14·6 c.c. N_2 (moist) at 18·5° and 764·5 mm. N=17·45.
$C_9H_{11}O_5N_3$ requires C=44·78; H=4·60; N=17·43 per cent.

The properties of the compound, as described below, must be understood to refer to both the quinole and quinone-ammonium forms, since the latter is readily convertible into the former by rehydration, and both forms pass into the normal ammonium type on conversion into salts. The ochreous quinonoid compound slowly becomes red in contact with cold water, this conversion into the quinole also taking place immediately when the compound is treated with hot water. It is of interest to place on record the fact that the reverse change—conversion into the quinonoid form—is brought about immediately by a strong aqueous solution of hydrazine, which in this case appears to act simply as a dehydrating agent.

The salts of this compound exist only in presence of an excess of the acid; they are readily dissociable by water or by exposure to the air, and no satisfactory analytical results could be obtained. The *bromide* is formed when the base is dissolved in concentrated hydrobromic acid solution, and crystallises in colourless, prismatic needles on adding alcohol and ether. An air-dried specimen contained Br = 23·24, whereas theory requires Br = 24·82 per cent.

The *nitrate* separates in colourless prisms from a solution of the compound in hot dilute nitric acid; it dissociates into the red quinole immediately on washing with water. An *iodide* crystallising in large, ochreous scales, which are brown by transmitted light, is formed by dissolving the base in hydriodic acid (D 1·5) and adding boiling alcohol to the solution; the salt crystallises out on cooling. A specimen washed with alcohol and ether and allowed to dry in the air gave results indicating that a periodide had been formed:

0·140 gave 0·1539 AgI. I = 59·39.
0·1160 „ 6·55 c.c. N_2 (moist) at 18·5° and 752·4 mm. N = 6·44.
$C_9H_{12}O_5N_3I,I_2$ requires I = 61·13; N = 6·74 per cent.

The general characters of this salt accord well with the view that it is a periodide, the low percentage of iodine being due to dissociation. Attempts to purify it by recrystallisation led to further dissociation.

A *platinichloride* crystallises out in pale, ochreous scales when a solution of platinic chloride is added to a solution of the chloride. These crystals change on exposure to the air into minute, ochreous needles, analyses of which indicated that dissociation had taken place. (Found, Pt = 20·18 and 20·09, instead of 21·85 per cent.)

Demethylation of the Quinone-ammonium Compound.—The study of the action of hydriodic acid on this compound led to the discovery that the methyl groups are not so readily eliminated as in the corresponding compound from picramic acid. This result is quite in harmony with the general principle that displaceable groups are more easily removed from the ortho- than from the para-position:

0·1039, when heated in a current of carbon dioxide with 15 c.c. hydriodic acid (D 1·5) and 5 grams of ammonium iodide to 205—210° for two and a-half hours, gave AgI = 0·1987. Me = 12·20.
$C_9H_{11}O_5N_3 - 2Me$ requires a loss = 12·46 per cent.

From this result it appears that demethylation in this case extends only to two methyl groups, the product no doubt being the monomethyl derivative of *iso*picramic acid, previously referred to as a product of direct methylation.

On heating the compound with concentrated hydrochloric acid to 135—140° in a sealed tube for four to five hours, demethylation to the extent of one methyl group takes place, the product consisting of the dimethyl*iso*picramic acid previously described. This was isolated by diluting the acid solution with water, filtering, and adding ammonia in excess to the acid filtrate. After the removal by filtration of the unchanged quinone-ammonium compound, the dimethyl*iso*picramic acid was precipitated by neutralisation with acetic acid, and identified by its melting point (182—183°) and conversion into its acetyl derivative (m. p. 156—158°):

0·1260 gave 16·8 c.c. N_2 (moist) at 18·5° and 765·7 mm. N = 15·47.

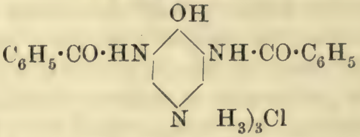
$C_{10}H_{11}O_6N_3$ requires N = 15·61 per cent.

Synthesis from p-*Hydroxyphenyltrimethylammonium Salts.*—The compound was prepared by the methylation of *p*-aminophenol in methyl-alcoholic solution by methyl iodide and potassium hydroxide according to the method of Griess. The iodide, nitrate, and free base all give the dinitroquinone-ammonium compound on nitration with fuming nitric acid under all conditions. Many attempts were made to arrest the nitration so as to obtain a mononitro-derivative, but without success; the compound either fails to nitrate or passes at once to the dinitro-derivative.

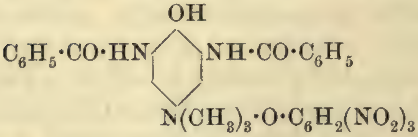
Reduction of the Dinitroquinone-ammonium Compounds.

The formula assigned to these compounds indicates that diaminohydroxyphenyltrimethylammonium salts might be expected to result from their complete reduction. The compound from *iso*picramic acid was reduced by adding the substance in small portions to a warm solution of stannous chloride containing tin and hydrochloric acid, and completing the reduction in the usual way. A white double salt appears to be formed on first introducing the substance into the stannous chloride solution, but this dissolves as the reduction proceeds. After removal of the tin as sulphide and evaporation of the solution, a white, crystalline chloride was obtained, but this was too soluble to be conveniently dealt with. The free base liberated by the action of alkali was also extremely soluble in water. The whole product was then benzoylated by the Schotten-Baumann method, and the resinous product collected and washed free from alkali. At this stage the product no doubt consists of the tribenzoyl derivative, but as the compound was resinous and uncrystallisable it was partly hydrolysed by boiling with alcoholic sodium hydroxide until a phenolic compound was obtained, the removal of the *O*-benzoyl group being thus indicated. The compound proved to be the expected 2:6-*di*-

benzoyldiamino-1-*hydroxyphenyl*-4-*trimethylammonium hydroxide.* The free base is a resinous substance, and could not be crystallised, but the salts are beautifully crystalline. The *chloride* (I) crystallises from hot water in large, silvery scales melting at 159°:



(I.) M. p. 159°.



(II.) M. p. 206—207°.

0·5941 gave 0·1941 AgCl. Cl = 8·07.

0·1719 „ 14·47 c.c. N_2 (moist) at 17° and 743·6 mm. N = 9·55.

$C_{23}H_{24}O_3N_3Cl,H_2O$ requires Cl = 7·99; N = 9·47 per cent.

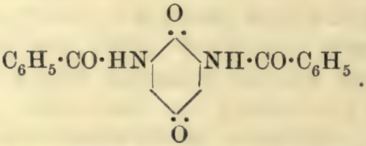
The *picrate* (II) was prepared by basifying the chloride with sodium carbonate, dissolving the base in alcohol, and adding to the solution an alcoholic solution of picric acid. The salt crystallises on cooling in yellow needles melting when pure at 206—207°:

0·0938 gave 0·1936 CO_2 and 0·0377 H_2O. C = 56·29; H = 4·46.

0·1216 „ 14·25 c.c. N_2 (moist) at 16·5° and 760·8 mm. N = 13·64.

$C_{29}H_{26}O_{10}N_6$ requires C = 56·28; H = 4·23; N = 13·59 per cent.

An attempt to prepare the nitrate by dissolving the base in hot dilute nitric acid led to the formation of an insoluble compound having none of the properties of a salt. After crystallisation from dilute acetic acid it consisted of dark ochreous needles melting at 232—233°. The analytical results indicated that the nitric acid in this case acts as an oxidising agent, removing the trimethylammonium group and giving rise to the formation of 2:6-*dibenzoyldiamino*-p-*benzoquinone*:

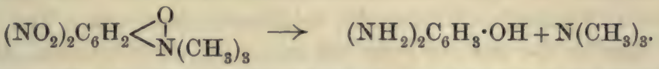


0·0710 gave 0·1802 CO_2 (H_2O lost). C = 69·22.

0·0863 „ 6·2 c.c. N_2 (moist) at 16·5° and 760·1 mm. N = 8·35.

$C_{20}H_{14}O_4N_2$ requires C = 69·33; N = 8·09 per cent.

The dinitroquinone-ammonium compound from picramic acid on reduction by tin and hydrochloric acid gave a product which indicated that in this case the reduction proceeds further than with the isomeride from *iso*picramic acid. The proximity of the trimethylammonium group to the hydroxyl so weakens the attachment of the former that complete elimination takes place with the formation of diaminophenol:



$$(NO_2)_2C_6H_2{<}\begin{matrix}O\\|\\N(CH_3)_3\end{matrix} \rightarrow (NH_2)_2C_6H_3\cdot OH + N(CH_3)_3.$$

The *m*-diaminophenol thus formed was identified by its colour reaction with nitrous acid, by the isolation of the hydrochloride, $C_6H_7ON_2,2HCl$, and by conversion into benzoyl derivatives. The latter were prepared by evaporating the acid solution to a small volume after removal of the tin as sulphide, and benzoylating with excess of benzoyl chloride in alkaline solution. The insoluble product, consisting of the *tribenzoyl* derivative,

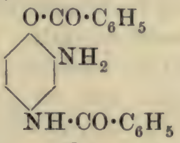
$$(NH\cdot CO\cdot C_6H_5)_2C_6H_3\cdot O\cdot CO\cdot C_6H_5,$$

was crystallised from dilute acetic acid, and obtained as a white, microcrystalline substance melting at 240—242°:

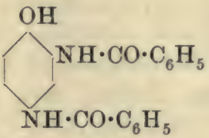
0·0986 gave 5·5 c.c. N_2 (moist) at 14° and 770·3 mm. N = 6·65.

$C_{27}H_{20}O_4N_2$ requires N = 6·42 per cent.

The tribenzoyl derivative on hydrolysis by heating for a short time with alcoholic sodium hydroxide gives the phenolic dibenzoyl derivative, together with a small quantity of a non-phenolic isomeride possessing basic properties. The latter was not obtained in sufficient quantity to examine in detail, but it most probably consists of the 4-benzoylamino-1-benzoyloxy-derivative (I), the other compound, forming the main product, being 2:4-*dibenzoyldiaminophenol* (II):



(I.)



(II.)

The latter crystallises from dilute alcohol in minute, grey scales melting at 253—254°:

0·1506 gave 11 c.c. N_2 (moist) at 16·5° and 765·5 mm. N = 8·55.

$C_{20}H_{16}O_3N_2$ requires N = 8·43 per cent.

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XCIV.—*Nickelo- and Palladio-dithio-oxalic acids.*

By Humphrey Owen Jones and Charles Stanley Robinson.

In a former paper (this vol., p. 62) the preparation and properties of a number of highly coloured salts derived from the complex nickelo- and palladio-dithio-oxalic acids were described. The salts were found to be derived from dibasic acids, $M''(COS)_4H_2$, dilute aqueous solutions of which had a higher electrical conductivity than equivalent solutions of sulphuric acid. The solutions when heated decomposed and lost their colour; attempts to evaporate the solvent under diminished pressure in the cold also resulted in partial decomposition. Finally, however, these difficulties were overcome, both acids were isolated in well-defined crystals, and their properties have been studied.

Nickelodithio-oxalic Acid, $Ni(COS)_4H_2,4H_2O$.

The barium salt, $Ni(COS)_4Ba,4H_2O$, in quantities of about 1 gram at a time was finely powdered and stirred with the calculated quantity of a 3*N*-solution of sulphuric acid, the solution was filtered through a Gooch crucible, placed in a flat dish in a vacuum desiccator over quicklime, and allowed to remain until most of the solvent had evaporated. Long, lustrous, black prisms, often exceeding 1 centimetre in length, were thus obtained:

0·4031 gave 0·1900 CO_2 and 0·0920 H_2O. C = 12·85; H = 2·54.
0·3320 „ 0·8305 $BaSO_4$. S = 34·6.

$Ni(COS)_4H_2,4H_2O$ requires C = 12·87; H = 2·68; S = 34·3 per cent.

The acid dissolves readily in water, giving the characteristic, deep magenta-coloured solution like the metallic salts previously described. The solution is strongly acid; on addition of barium chloride the barium salt is precipitated, and on addition of ammonium carbonate the ammonium salt is precipitated and carbon dioxide is evolved. On heating the solution of the acid, the colour disappears, hydrogen sulphide and carbon monoxide are evolved, a green precipitate of nickel oxalate separates, and the solution was found to contain oxalic acid.

Quantitative experiments showed that on boiling the solution 1 gram-molecule of the acid gave 4 gram-molecules of hydrogen sulphide and 1 gram-molecule of nickel oxalate, but that the relative quantities of oxalic acid and carbon monoxide were variable. In solutions of about normal strength 1 gram-molecule of acid gave 0·5 gram-molecule of oxalic acid and 0·5 gram-molecule of carbon monoxide; but in approximately decinormal solution the decomposition was much less rapid, and the proportion of oxalic acid rose to about 0·7 gram-molecule and the carbon monoxide fell to about 0·3 gram-molecule.

The following experiments illustrate the kind of result obtained:

0·8945 Gram of the barium salt (molecular weight 508), when heated with the calculated quantity of *N*/10-sulphuric acid, gave 9·0 c.c. of carbon monoxide at 17° and 770 mm. measured over potassium hydroxide solution; that is, 6·34 litres per gram-molecule. The oxalic acid required 23·3 c.c. of potassium permanganate solution (1 c.c. = 0·00353 gram), and the nickel oxalate required 31·2 c.c. of the same solution for oxidation.

Hence the free oxalic acid is 66·6 grams and the oxalic acid as nickel oxalate is 89·1 grams per gram-molecule of salt.

The sum of the carbon monoxide and the oxalic acid is, therefore, 1·02 gram-molecules per gram-molecule of salt.

A similar experiment gave 0·315 gram-molecule of carbon monoxide, 0·703 gram-molecule of oxalic acid, and 90·3 grams of oxalic acid as nickel oxalate.

Two experiments in which the calculated quantity of *N*-sulphuric acid was used gave 0·482 and 0·509 gram-molecule of carbon monoxide with 0·55 and 0·51 gram-molecule of oxalic acid respectively, whilst both gave practically 1 gram-molecule of nickel oxalate. The sum of the carbon monoxide and oxalic acid is therefore practically 1 gram-molecule in each case.

Two experiments gave as a mean 4·1 gram-molecules of hydrogen sulphide from 1 gram-molecule of salt.

These results are in agreement with the following equations for the decomposition of the acid:

$$H_2(COS)_4Ni + 4H_2O = 4H_2S + H_2C_2O_4 + NiC_2O_4.$$
$$H_2(COS)_4Ni + 3H_2O = 4H_2S + CO + CO_2 + NiC_2O_4.$$

The two modes of decomposition take place in different proportions according to the concentration of the solution.

It is probable that the decomposition of the radicle of dithio-oxalic acid takes place, giving different proportions of oxalic acid and its decomposition products—carbon monoxide and carbon dioxide—according to the concentration.

The decomposition of the acid by heat was examined by heating the acid to about 180—200° in a vacuous bulb, and collecting the gas evolved by means of a Töpler pump.

The following experiment is typical:

0·0960 Gram gave 28·6 c.c. of gas at 17° and 766 mm. (=106 litres per gram-molecule), of which 12·0 c.c. remained after treatment with potassium hydroxide solution (=43·7 litres per gram-molecule).

The decomposition may therefore be represented by the equation:

$$Ni(COS)_4H_2,4H_2O = NiS + 2CO + 2COS + H_2S + 4H_2O,$$

which differs slightly from that which represents the decomposition of the aniline salt (*loc. cit.*, p. 70).

The electrical conductivity of a solution of this acid was measured, and found to be slightly greater than that already recorded (*loc. cit.*, p. 71) from solution prepared by mixing equivalent solutions of the barium salt and sulphuric acid. This is probably to be attributed to the presence of small quantities of oxalic acid in the free acid; the values previously given are therefore to be regarded as the more trustworthy, and show that this acid is probably stronger than sulphuric acid.

Several attempts were made to prepare the ester of the acid by the interaction of the potassium salt and methyl sulphate. On heating the two substances together in the presence of water, nickel sulphate, hydrogen sulphide, and dimethyl dithio-oxalate were obtained. On warming the dry potassium salt with methyl sulphate in a sealed tube, a deep blue-coloured mass was obtained, from which dry acetone extracted a coloured substance mixed with some dimethyl dithio-oxalate, and much unchanged potassium salt was left; heating for a longer time resulted in decomposition with loss of the colour.

Methyl sulphate was found to react slowly with the dry potassium salt in the cold, but even after keeping for six months in a sealed tube the reaction was incomplete. The excess of methyl sulphate was removed by means of dry ether, and the residue was extracted repeatedly with dry acetone. On evaporating the acetone in the cold, deep indigo-blue, feathery needles were deposited, mixed with a few red octahedra of the potassium salt. Analysis gave results approximating to the composition of the half ester, $Ni(COS)_4KMe$, but no method of separating this from the unchanged potassium salt has been found.

This substance when heated evolved dimethyl dithio-oxalate.

Palladiodithio-oxalic Acid, $Pd(COS)_4H_2,3H_2O$.

This acid is more soluble in water than the corresponding nickelo-acid, but the same method served for its preparation. Crystals of oxalic acid were sometimes observed mixed with the crystals of the acid if the evaporation had not been carried out rapidly enough. The acid separates from its solution in small, dark brown plates:

0·3155 gave 0·1390 CO_2 and 0·0545 H_2O. C=12·0; H=1·92.
0·3090 „ 0·1361 CO_2 „ 0·0521 H_2O. C=12·0; H=1·87.
0·2160 „ 0·5053 $BaSO_4$ and 0·0585 Pd. S=32·1; Pd=27·0.
$Pd(COS)_4H_2,3H_2O$ requires C=11·94; H=1·98; S=31·84; Pd=26·4 per cent.

The solution of the acid in water is dark brown in colour, strongly acid to indicators, gives a precipitate of the barium salt with barium chloride, and liberates carbon dioxide from ammonium carbonate with precipitation of the ammonium salt.

On heating, the solution gradually becomes colourless, hydrogen sulphide and carbon monoxide are evolved together with some carbon dioxide, and the residue consists mainly of palladium.

The expenses of this work were partly defrayed by a grant from the Government Grant Committee of the Royal Society, for which we are glad to make this grateful acknowledgment.

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XCV.—*Dithiomalonates.*

By HUMPHREY OWEN JONES and CHARLES STANLEY ROBINSON.

IT has been shown (Jones and Tasker, Trans., 1909, **95**, 1904; Robinson and Jones, this vol., p. 62) that when certain metallic salts are added to solutions of dithio-oxalates, intense colours are produced, and that the production of these colours is due to the formation of complex acid ions. It seemed of interest to prepare thiomalonates and thiosuccinates, and to compare their properties with those of the thio-oxalates and the properties and colours of complex thiomalonates, thiosuccinates, and thiocarbonates, if formed, with those of the complex thio-oxalates previously described. This paper contains an account of the study of the derivatives of dithiomalonic acid, $CH_2(CO\cdot SH)_2$.

It was found that when the theoretical quantity of amyl mercaptan was added to malonyl chloride, interaction took place with the formation of a pale yellow oil, and hydrogen chloride was evolved. In order to purify this oil it was distilled in a vacuum, but decomposition took place with the formation of a large quantity of a red solid, which appeared to have the composition and properties of polymerised carbon suboxide, $(C_3O_2)_x$ (Diels and Wolf, *Ber.*, 1906, **39**, 689). The same kind of decomposition was observed to a less extent in the case of ethyl dithiomalonate (Purvis, Jones, and Tasker, Trans., 1910, **97**, 2289). Consequently, the oil could not be obtained pure, and as distillation involved considerable loss, for the purposes of this investigation it was sufficient to remove the dissolved hydrogen chloride by allowing the oil to remain over lime in a vacuum.

Potassium Dithiomalonate, $CH_2(CO\cdot SK)_2$.—The amyl dithiomalonate was saponified by heating on the water-bath with the theoretical quantity of alcoholic *N*-potassium hydrosulphide for about an hour, and then allowing to remain in the cold. After a few days potassium dithiomalonate separated in long, colourless needles:

0·2145 gave 0·1330 CO_2 and 0·020 H_2O. C=16·90; H=1·04.
0·2280 „ 0·5065 $BaSO_4$. S=30·5.
$C_3H_2O_2S_2K_2$ requires C=16·93; H=0·95; S=30·2 per cent.

The behaviour of aqueous solutions of this salt towards various metallic salts was next examined.

Lead Acetate.—Yellow precipitate which blackens on keeping.

Mercuric Chloride.—Yellow precipitate soluble in excess of thiomalonate, which does not change much in appearance on boiling.

Mercurous Nitrate.—Black precipitate.

Silver Nitrate.—Yellow precipitate which blackens on keeping.

Copper Sulphate.—Yellow precipitate which blackens on heating.

Nickel Chloride.—Claret coloration.

Cobalt Chloride.—Green coloration with separation of sulphide.

Calmium Chloride.—Yellow precipitate.

Palladium Chloride.—Intense yellow coloration. If excess of palladium chloride is added, carbon monoxide is evolved, and palladium disulphide separates.

Ferrous Sulphate.—Reddish-purple coloration.

Bismuth, antimony, and tin give precipitates of the sulphides on boiling.

Aqueous solutions of potassium dithiomalonate thus behave in a similar manner to solutions of potassium dithio-oxalate. Colours are developed with solution of nickel, cobalt, palladium, and iron salts, and these colours, as will be shown later in two cases, are due to the formation of complex acid ions containing metal.

Reaction with Aniline Hydrochloride.—On mixing concentrated solutions of potassium dithiomalonate and aniline hydrochloride in the cold, a brisk effervescence due to evolution of hydrogen sulphide sets in immediately, and lustrous plates separate from the solution. These crystallised from alcoholic solution in needles melting at 222—223°, and proved to be malonanilide.

This reaction is similar to the decomposition of aniline dithiooxalate (*loc. cit.*, p. 64).

Nickelodithiomalonates.

Potassium Nickelodithiomalonate, $Ni[(COS)_2CH_2]_2K_2$.—When solutions of nickel chloride and potassium dithiomalonate are mixed, a claret coloration is developed. This colour persists at great dilution, being appreciable at a dilution of 1 part of nickel in 4,000,000 of water. The colour of the corresponding nickelothiooxalate is perceptible at a dilution of 1 part of nickel in 40,000,000 of water. On mixing concentrated solutions of nickel chloride and potassium dithiomalonate, a red, crystalline precipitate separates. This salt dissolves in hot water, from which it crystallises on cooling in small, brick-red, flat-sided prisms:

0·3132 gave 0·1995 CO_2 and 0·0307 H_2O. C=17·3; H=1·08.
0·2560 „ 0·5940 $BaSO_4$. S=31·84.
$C_6H_4O_4S_4K_2Ni$ requires C=17·7; H=0·99; S=31·62 per cent.

Barium Nickelodithiomalonate.—This salt separates in long needles when barium chloride is added to a concentrated solution of potassium nickelodithiomalonate. When exposed to air the crystals lose weight, and when dried in a desiccator over calcium chloride they lose water and become green. If these green crystals are moistened with water and allowed to dry in the open air, they become red once more. The change in colour is therefore due to dehydration.

The red salt was analysed with the following results:

0·4320 gave 0·1950 CO_2 and 0·1070 H_2O. C=12·3; H=2·7.
0·4806 „ 0·1922 $BaSO_4$. Ba=23·5.
$C_6H_4O_4S_4BaNi,6H_2O$ requires C=12·6; H=2·8; Ba=23·9 per cent.

The green salt obtained after allowing the red salt to remain in a desiccator over calcium chloride for several days gave the following results on analysis:

0·5040 gave 0·2680 CO_2 and 0·0465 H_2O. C=14·5; H=1·02.
0·5342 „ 0·2855 CO_2 „ 0·0535 H_2O. C=14·5; H=1·1.
0·4973 „ 0·2445 $BaSO_4$. Ba=28·9.
$C_6H_4O_4S_4BaNi,2H_2O$ requires C=14·4; H=1·6; Ba=27·6 per cent.
$C_6H_4O_4S_4BaNi,1H_2O$ „ C=15·0; H=1·25; Ba=28·7 „ „

The salt is therefore most probably the monohydrate. The same monohydrate is obtained by treatment of the red salt with alcohol and removal of the alcohol in a desiccator.

Aniline Nickelodithiomalonate.—This salt separates in chocolate-brown needles when a solution of aniline hydrochloride is added to one of potassium nickelodithiomalonate:

0·2542 gave 0·3790 CO_2 and 0·0870 H_2O. C=40·69; H=3·8.
0·3002 „ 0·5314 $BaSO_4$. S=24·30.
$C_6H_4O_4S_4Ni(C_6H_5{\cdot}NH_3)_2,H_2O$ requires C=40·53; H=3·8; S=24·0 per cent.

Palladiodithiomalonates.

Potassium Palladiodithiomalonate, $Pd[(COS)_2CH_2]_2K_2$.—When a concentrated solution of palladium chloride is added slowly with stirring to a strong solution of potassium dithiomalonate, a yellow, crystalline salt separates. The addition of palladium chloride is continued until the liquid darkens in colour. Beyond this point further addition of palladium chloride causes decomposition, with separation of palladium disulphide.

The crystalline precipitate, after being collected and recrystallised from hot water, separates in pale yellow plates:

0·4145 gave 0·2315 CO_2 and 0·0370 H_2O. C=15·25; H=0·90.
0·2445 „ 0·5105 $BaSO_4$. S=28·65.
$C_6H_4O_4S_4K_2Pd$ requires C=15·7; H=0·89; S=28·3 per cent.

Barium palladiodithiomalonate separates in long, yellow prisms when a solution of barium chloride is added to one of potassium palladiodithiomalonate.

Aniline Palladiodithiomalonate.—This salt separates in long needles or lustrous, hexagonal plates on adding a solution of aniline hydrochloride to a solution of potassium palladiodithiomalonate:

0·2445 gave 0·3400 CO_2, 0·0835 H_2O, and 0·0465 Pd. C=37·90; H=3·79; Pd=19·0.
$C_6H_4O_4S_4Pd(C_6H_5{\cdot}NH_3)_2$ requires C=38·4; H=3·56; Pd=18·6 per cent.

The free nickelo- and palladio-thiomalonic acids are less stable than the corresponding thio-oxalic acids, and have hitherto not been obtained in a pure state.

The expenses of the work have been largely defrayed by grants from the Government Grant Committee of the Royal Society, for which we are glad to make this grateful acknowledgment.

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XCVI.—*The Resolution of Benzoylalanine into its Optically Active Components.*

By **William Jackson Pope** and **Charles Stanley Gibson.**

A considerable number of applications have been made of the equilibrium method of resolving externally compensated bases into their optically active components first introduced by Pope and Peachey (Trans., 1899, **75**, 1066); several modes of putting the method into practice have been successfully employed. One of these consists in dissolving in an appropriate solvent two equivalents of the externally compensated base $dBlB$, rather more than one equivalent of an optically inactive acid, say, hydrochloric, and a correspondingly smaller quantity of an optically active acid, dA, and causing the mixture to crystallise, care being taken that the optically inactive acid used is one which gives a very soluble salt with the base. If the salt $dBdA$ is the least soluble of which the formation is possible in the system, equilibrium is reached after crystallisation when the maximum quantity of this salt has become deposited, provided that the salt $dBdA$ does not form an isomorphous mixture with the salt $lBdA$. The change is represented by the equation:

$$dBlB + dA + \mathrm{HCl} = lB,\mathrm{HCl} + dBdA,$$

the salt lB,HCl remaining wholly in solution and the major portion of the salt $dBdA$ crystallising out. Other modes of applying the equilibrium method readily suggest themselves, and have been adopted with success (Pope and Rich, Trans., 1899, **75**, 1093; Pope and Read, Trans., 1910, **97**, 2199).

The method should also be applicable to the resolution of externally compensated acids, and could be applied by dissolving two equivalents of the externally compensated acid $dAlA$, rather more than one equivalent of an optically inactive base, say, potassium hydroxide, and a correspondingly smaller proportion of an optically active base, dB, in the same solution; on causing crystallisation to occur, the salt $dBdA$ would separate if it happened to be the most sparingly soluble salt of which the formation was possible. The change would proceed in accordance with the equation:

$$dAlA + dB + \mathrm{KHO} = lA,\mathrm{KHO} + dBdA,$$

the potassium salt of the lævo-acid remaining wholly in solution provided it were sufficiently soluble.

The equilibrium method has hitherto only been applied to the resolution of externally compensated acids in the case of 1-methyl*cyclo*hexylidene-4-acetic acid (Perkin, Pope, and Wallach, Trans., 1909, **95**, 1789), and, although it proved highly successful, the results were complicated by the formation of an isomorphous mixture between the two salts *dBlA* and *dBdA*. It therefore seemed desirable to further test the applicability of the equilibrium method to the resolution of externally compensated acids, and consequently we have carefully studied the manner in which the method can be used in the resolution of externally compensated benzoylalanine.

Resolution of Externally Compensated Benzoylalanine.

Externally compensated benzoylalanine was prepared by Fischer (*Ber.*, 1899, **32**, 2454), who resolved it into its optically active components by crystallisation with an equivalent quantity of brucine; the brucine salt of *l*-benzoylalanine was thus first separated, and the *d*-isomeride was subsequently isolated as its strychnine salt from the acid remaining in the mother liquors. As the result of a number of preliminary experiments we found that the strychnine salt of *d*-benzoylalanine is much less soluble in water than the brucine salt of *l*-benzoylalanine; it follows that in carrying out the resolution the externally compensated benzoylalanine should be first treated with strychnine, and the *l*-acid afterwards separated with the aid of brucine.

In applying the equilibrium method, two equivalents of *dl*-benzoylalanine (25 grams), one equivalent of potassium hydroxide (3·69 grams) in normal aqueous solution, and one equivalent of strychnine (21·1 grams) are dissolved in a sufficiency of boiling water, and the solution allowed to remain in a cool place, preferably after inoculating with a little of the crystalline salt of strychnine and *d*-benzoylalanine. Practically the theoretical quantity of the latter salt separates, on well cooling, in large, characteristic, colourless prisms.

Strychnine d-*Benzoylalanine*, $C_{21}H_{22}O_2N_2,C_{10}H_{11}O_3N,2H_2O$.

When separated as above described, this salt is pure except for contamination with included mother liquor; the latter is completely removed by one recrystallisation from boiling water, but the quantitative results quoted below refer to salt which had been recrystallised three times. The substance is very sparingly soluble in cold water, and melts at 129° with rapid loss of water of crystallisation:

0·1300 gave 0·3130 CO_2 and 0·0801 H_2O. $C = 65·60$; $H = 6·90$.
0·1200 „ 0·2885 CO_2 „ 0·0735 H_2O. $C = 65·56$; $H = 6·86$.
0·4745 lost 0·0286 at 100°. $H_2O = 6·03$.
$C_{31}H_{37}O_7N_3$ requires $C = 66·04$; $H = 6·62$; $2H_2O = 6·40$ per cent.

The rotation constants were determined in dilute aqueous solution. 0·1088 Gram, made up to 29·94 c.c. with water, gave the following results in a 4-dcm. tube at 20°:

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α	− 0·175°	− 0·165°	− 0·155°
$[\alpha]$	12·04	11·35	10·66
$[M]$............	67·8	63·9	60·0

Rotatory dispersions : $Hg_{green}/Na_{yellow} = 1·129$; $Hg_{yellow}/Na_{yellow} = 1·064$.

Brucine l-*Benzoylalanine*, $C_{23}H_{26}O_4N_2,C_{10}H_{11}O_3N,4\frac{1}{2}H_2O$.

The collected mother liquors remaining after the separation and purification of the strychnine *d*-benzoylalanine are evaporated to one-half their bulk, concentrated potassium hydroxide solution added, and the precipitated strychnine removed; the crude *l*-benzoylalanine is then precipitated from the filtrate by addition of concentrated hydrochloric acid. The rotatory power of the acid thus obtained is determined in order that the percentage of pure *l*-acid contained in it may be calculated; in the subsequent treatment the crude *l*-acid is dissolved in water with the addition of amounts of potassium hydroxide corresponding with the *d*-acid present and of brucine corresponding with the quantity of *l*-acid found. A typical case is next described.

The crude precipitated *l*-acid, in the form of its potassium salt, was found to have the specific rotatory power $[\alpha]_{Hg\ green} - 28·34°$; this value corresponds with the presence of 85 per cent. of the pure *l*-acid. The crude *l*-acid (13·5 grams) was consequently brought into solution in boiling water with the addition of brucine (27·5 grams) and potassium hydroxide (0·609 gram); after remaining in a cool place for some time the brucine salt separated in minute, crystalline plates, and an almost quantitative yield was obtained. One recrystallisation from boiling water serves to eliminate adherent mother liquor, but the quantitative data given below were obtained with salt which had been recrystallised four times; the pure salt melts at 89—91° in its water of crystallisation:

0·2048 gave 0·4445 CO_2 and 0·1305 H_2O. $C = 59·20$; $H = 7·13$.
0·2144 „ 0·4665 CO_2 „ 0·1320 H_2O. $C = 59·29$; $H = 6·89$.
0·5446 lost 0·0652 at 105°. $H_2O = 11·97$.
$C_{33}H_{37}O_7N_3,4\frac{1}{2}H_2O$ requires $C = 59·24$; $H = 6·94$;
$4\frac{1}{2}H_2O = 12·12$ per cent.

The following determinations of the rotation constants were made. 0·3117 Gram, made up to 29·94 c.c. with water, gave, in a 4-dcm. tube at 20°:

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α	− 1·73°	− 1·46°	− 1·40°
[α]	41·5	35·1	33·6
[M]............	278	234	225

Rotatory dispersions : Hg_{green}/Na_{yellow} = 1·236 ; Hg_{yellow}/Na_{yellow} = 1 044.

d- *and* l-*Benzoylalanine*, $CH_3 \cdot CH(CO_2H) \cdot NH \cdot CO \cdot C_6H_5$.

The *d*- and *l*-benzoylalanines are obtained from the corresponding strychnine and brucine salts by first separating the alkaloid by addition of potassium hydroxide solution, and then precipitating the acid from the filtrate by hydrochloric acid; they melt at 147—148°, as stated by Fischer. In view of the small amount of data available concerning the rotation constants of the optically active benzoylalanines, the following series of determinations were made with carefully purified specimens of the materials; in each case the weight of material stated was made up to 29·94 c.c. with the solvent, and the rotatory power determined in 4-dcm. tubes at 20°.

d-*Benzoylalanine.* l-*Benzoylalanine.*

As potassium salt in water:

	0·5238 gram + 5·5 c.c. *N*/2-KHO.			0·5162 gram + 5·5 c.c. *N*/2-KHO.		
	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α	+ 2·90°	+ 2·53°	+ 2·42°	− 2·85°	− 2·49°	− 2·36°
[α]	41·4	36·1	34·6	41·3	36·1	34·2
[M]......	80·0	69·8	66·8	79·8	69·7	66·1

Rotatory dispersions : 1·198 ; 1·046. 1·205 ; 1·055.

	2·5460 grams + 26·4 c.c. *N*/2-KHO in 2-dcm. tube.			2·6760 grams + 27·7 c.c. *N*/2-KHO in 2-dcm. tube.		
α	+ 7·42°	+ 6·47°	+ 6·18°	− 7·84°	− 6·83°	− 6·50°
[α]	43·6	38·6	36·3	43·8	38·2	36·4
]M]......	84·3	73·4	70·2	84·7	73·8	70·2

Rotatory dispersions : 1·201 ; 1·047. 1·203 ; 1·051.

In aqueous solution:

	0·3066 gram.			0·3076 gram.		
α	+0·13°	+0·11°	+0·10°	−0·13°	−0·11°	−0·10°
[α]	3·2	2·7	2·4	3·2	2·7	2·4
[M]......	6·1	5·2	4·7	6·1	5·2	4·7

Rotatory dispersions : 1·300 ; 1·100. 1·300 ; 1·100.

d-*Benzoylalanine.*

	1·0094 grams in alcohol.			1·0163 grams in acetone.		
α	+ 1·71°	+ 1·47°	+ 1·41°	+ 4·10°	+ 3·54°	+ 3·38°
$[\alpha]$	12·7	10·9	10·5	30·2	26·1	24·9
$[M]$......	24·5	21·1	20·2	58·3	50·4	48·1
Rotatory dispersions :	1·213 ; 1·043.			1·213 ; 1·047.		

It will be seen that the rotatory power of benzoylalanine in the form of its potassium salt in aqueous solution increases with the concentration; this is confirmed by Fischer's observation that the *l*-acid gives the value $[\alpha]_D$ −37·13° in a more concentrated solution than was used by us. The rotatory dispersion is practically independent of the concentration. The very high values for the rotation constants obtained in acetone solution are noteworthy. No mutarotation was observed with any of the solutions.

The method which is described in the previous pages is obviously a very convenient one for the complete separation of externally compensated benzoylalanine into its optically active components.

Treatment of dl-*Benzoylalanine with Brucine.*

As was anticipated from the fact that the strychnine salt of *d*-benzoylalanine is more sparingly soluble than is the brucine salt of the *l*-isomeride, the resolution of the externally compensated acid is most readily effected by first separating the *d*-acid as strychnine salt and afterwards isolating the *l*-isomeride as brucine salt. The attempt to apply the equilibrium method in the reverse way, by treating first with brucine and subsequently with strychnine, led to an interesting complication, and may therefore be described.

Two equivalents of *dl*-benzoylalanine (80 grams), one of brucine (96·6 grams), and one of potassium hydroxide (11·6 grams) are dissolved in a sufficient quantity of boiling water, and the clear solution allowed to remain for twelve hours in a cold storage chamber. A copious, crystalline deposit is obtained (125 grams), which is separated and recrystallised from boiling water.

The substance obtained in this manner crystallises much more satisfactorily than does the pure brucine *l*-benzoylalanine described above; it forms colourless, glistening plates, which melt at 92—93° in their water of crystallisation, and exhibit a more macrocrystalline character than do the crystalline fragments of that pure salt. The substance exhibits rotation constants which are not altered by crystallisation from boiling water, and the following data were obtained with material which had been crystallised four times from that solvent; 0·3202 gram, made up to 29·94 c.c. with water, gave the appended values in a 4-dcm. tube at 20°:

	Hg_{green}	Hg_{yellow}	Na_{yellow}
α …………	− 1·46°	− 1·23°	− 1·18°
$[\alpha]$ …………	34·1	28·7	27·6
[M]…………	225	190	182

Rotatory dispersions: $Hg_{green}/Na_{yellow} = 1·238$; $Hg_{yellow}/Na_{yellow} = 1\ 042$.

On comparing these values with those given above for brucine *l*-benzoylalanine, it became clear that the latter is not identical with the substance now described; this conclusion is confirmed by the different melting points and rotation constants of the two materials.

On combustion and determination of the water of crystallisation, both salts gave the same results; as, however, the percentage compositions of the normal and acid salts of brucine with benzoylalanine do not differ greatly, the acid present in the salts was determined volumetrically, using phenolphthalein as the indicator, and it was found that both salts have the normal composition.

The acid liberated from the salt now under consideration gave a low rotation constant; 0·5210 gram, made up to 29·94 c.c. with 2·70 c.c. *N*-potassium hydroxide and water, gave $\alpha_{\text{Hg green}} - 2·74°$, whence $[\alpha]_{\text{Hg green}} - 39·4°$. It also had a low melting point, namely, 136—137°. It was therefore to be concluded that the salt really consisted of an isomorphous mixture of brucine *d*- and *l*-benzoylalanine, which could not be resolved by recrystallisation under the conditions employed; this case is, in fact, similar to that encountered by Perkin, Pope, and Wallach during the resolution of *dl*-1-methyl*cyclo*hexylidene-4-acetic acid by crystallisation with strychnine (Trans., 1909, **95**, 1789). This conclusion indicates that brucine *d*-benzoylalanine is a crystalline substance, and in confirmation of this it was found that the latter salt crystallises readily.

Brucine d-*Benzoylalanine*, $C_{23}H_{26}O_4N_2,C_{10}H_{11}O_3N,5H_2O$.

Molecular proportions of the component base and acid are dissolved in boiling water; on cooling, the salt separates as a felted mass of colourless needles, which melt in their water of crystallisation at 90°. The substance is very soluble in water:

0·1922 gave 0·4100 CO_2 and 0·1200 H_2O. C = 58·18; H = 6·99.

0·4912 lost 0·0646 at 105°. H_2O = 13·15.

$C_{33}H_{37}O_7N_3,5H_2O$ requires C = 58·45; H = 6·99; H_2O = 13·30 per cent.

The following determinations of rotatory power were made, 0·3412 gram being made up to 29·94 c.c. with water, and the solution examined in a 4-dcm. tube at 20°:

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α …………	− 1·28°	− 1·08°	− 1·00°
$[\alpha]$ …………	28·1	23·7	21·9
[M]…………	190	160	149

Rotatory dispersions : $Hg_{green}/Na_{yellow} = 1·280$; $Hg_{yellow}/Na_{yellow} = 1·080$.

A comparison of the rotation constants of the brucine salts of *d*- and *l*-benzoylalanine with those of the salt described above which yields the *l*-acid of low rotatory power, further confirms the conclusion that the latter salt is a mixture.

It may be noted that whilst externally compensated benzoylalanine melts at 160° and the pure optically active components at 147—148°, a mixture of either *d*- or *l*-benzoylalanine with 2·4 per cent. of its enantiomorphously related isomeride melts at 136°. The melting-point curve of mixtures of *d*- and *l*-benzoylalanine is thus of the type depicted in Roozeboom's Fig. 7 (*Zeitsch. physikal. Chem.*, 1899, **28**, 508), and the externally compensated substance must be regarded as a true racemic compound at the melting point.

p-*Toluenesulphonylalanine*, $CH_3·CH(CO_2H)·NH·SO_2·C_6H_4·CH_3$.

p-Toluenesulphonyl chloride reacts readily with *dl*-alanine, and gives a good yield of the sulphonyl derivative under the following conditions: One molecular proportion of alanine (5 grams), 2 molecular proportions of *p*-toluenesulphonyl chloride (21·4 grams), and three of potassium hydroxide (9·5 grams) are warmed together in presence of water (100 c.c.); the acid chloride and the potassium hydroxide should be added gradually, and the mixture finally left on the water-bath for some hours, by which time the excess of acid chloride is destroyed. The p-*toluenesulphonylalanine* separates on addition of hydrochloric acid, and is purified by recrystallisation from boiling water. It forms long, colourless needles melting at 138—139°, is almost insoluble in cold water, benzene, or ether, but dissolves readily in alcohol or acetone:

0·1565 gave 0·2815 CO_2 and 0·0745 H_2O. C = 49·06; H = 5·33.

$C_{10}H_{13}O_4NS$ requires C = 49·34; H = 5·39.

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XCVII.—*Nor-hyoscyamine and Nor-atropine; Alkaloids Occurring in Various Solanaceous Plants.*

By FRANCIS HOWARD CARR and WILLIAM COLEBROOK REYNOLDS.

VERY few instances have been recorded of secondary alkaloidal bases occurring in nature. It is therefore not surprising that whilst the alkaloid hyoscyamine, which is a monacidic tertiary base having a methyl group attached to the *N*-atom, is found in very many different plants, the occurrence of the homologous secondary base, nor-hyoscyamine, has not hitherto been observed. In the present communication the alkaloid nor-hyoscyamine, obtained during the preparation of large quantities of mydriatic bases, is described, and is shown to occur in four different species of the natural order Solanaceæ, namely, in *Scopolia japonica, Duboisia myoporoides, Datura metel*, and *Datura meteloides*, whilst its presence in *Mandragora vernalis* is proved by the evidence afforded that ψ-hyoscyamine (a supposed isomeride of hyoscyamine), which occurs in this plant, is identical with nor-hyoscyamine. In every case nor-hyoscyamine is accompanied by hyoscyamine. Just as the latter may be racemised to form atropine, so also nor-hyoscyamine is convertible into its racemic modification, nor-atropine—a base differing from it in physical and physiological properties alike.

The properties of these two bases and of their salts have been investigated, and the preparation of hyoscyamine and atropine by the methylation of the respective homologues has been accomplished.

In this way it has been clearly shown that the two new bases differ only from hyoscyamine and atropine respectively in that they are devoid of the methyl group attached to the nitrogen atom. In accordance with the nomenclature of other similarly related bases, the names nor-hyoscyamine and nor-atropine have therefore been adopted.

On hydrolysis nor-hyoscyamine yields tropic acid and a known base, nortropanol. Merling, who first prepared this substance, called it tropigenine; later, Ciamician and Silber named it tropoline, but Willstätter, in reviewing the nomenclature of this group of compounds, designated it nortropanol, which name the authors have adopted. It would, however, be more in accordance with the authors' wishes to adopt the new name, nortropine, for it.

Nor-hyoscyamine was first isolated by the authors from the rhizome of *Scopolia japonica.* The genus Scopolia includes two species, both closely resembling *Atropa belladonna*, and respectively indigenous in Europe and Japan. The European species, *S. carniolica,* has been subjected to fairly complete chemical investigation. The Japanese variety, however, *Scopolia japonica,* has received less attention. It differs from the European plant in the appearance of its rhizome and leaves. It is called by the Japanese "rôtô" or "hashiridokoro," and has for long been employed by them in medicine. It now figures as an official drug in the Japanese Pharmacopœia.

In 1878 G. Martin (*Arch. Pharm.*, **216**, 336) stated that the plant produces narcotic effects similar to, but less marked than, those of Belladonna. He recorded that he found solanine, but no atropine, in the plant.

In 1880 Langaard (*Pharm. J.*, 1880, [iii], **11**, 10) obtained from the rhizomes a small quantity of a crystalline alkaloid, which he named rotoine, but which he was unable to characterise owing to the small quantity at his disposal. He also obtained an amorphous alkaloid in larger amount, and this he named scopoleine, but he did not characterise it. Later, in 1884, J. F. Eykman (*Niew. Tydsch. Pharm.*, 1884, 154 and 177) confirmed Langaard's observations.

In 1888 Schmidt and Henschke (*Arch. Pharm.*, **226**, 185) submitted the total alkaloid obtained from the roots of this plant to a process of fractional precipitation as aurichloride. In this way they were enabled to identify hyoscyamine, atropine, and hyoscine aurichlorides.

No further work appears to have been published on the alkaloids of *Scopolia japonica* until 1909, when M. Watanabe (*Int. Cong. Appl. Chem. London*, 1909, VIII *B*, 135) found that the stem and leaves of this plant contain mydriatic alkaloids, which he indicated were almost certainly hyoscyamine, atropine, and scopolamine.

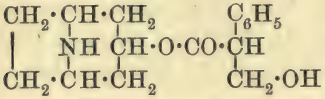
In the present investigation the dry rhizome of *Scopolia japonica* has yielded in a pure condition:

0·03 per cent. of nor-hyoscyamine.
0·15 „ „ hyoscyamine.

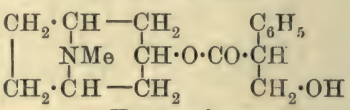
The separation of the two alkaloids was accomplished by a long and tedious process of fractional crystallisation of the salts of the mixture. No indication of the presence of hyoscine was obtained.

Nor-hyoscyamine, $C_{16}H_{21}O_3N$, is a white, crystalline base melting at 140·5°. It is strongly basic in character, even phenolphthalein being coloured by it. It forms beautifully crystalline salts, of which the following have been characterised: *hydrochloride,* $C_{16}H_{21}O_3N,HCl$; *sulphate,* $(C_{16}H_{21}O_3N)_2H_2SO_4,3H_2O$; *oxalate,* $(C_{16}H_{21}O_3N)_2,C_2H_2O_4$; *aurichloride,* $C_{16}H_{21}O_3N,HAuCl_4$; *platinichloride,* $(C_{16}H_{31}O_3N)_2,H_2PtCl_6,3H_2O$; and the *picrate.*

Its chemical relationship to hyoscyamine was proved: (1) by showing by the Herzig and Meyer method that the compound contained no *N*-CH_3 group; (2) by forming the nitrosoamine, thus showing it to be a secondary amine; (3) by acting on it with methyl iodide, forming *l*-hyoscyamine identical in every way with naturally occurring hyoscyamine; (4) by hydrolysing with barium hydroxide, and thus obtaining tropic acid and nortropanol. Its relation to hyoscyamine may therefore be expressed by the formulæ:



Nor-hyoscyamine.



Hyoscyamine.

The specific rotatory power of the basic ion in the salts of nor-hyoscyamine is $[\alpha]_D$ −33·8° in water, whilst the figure for the base dissolved in 50 per cent. ethyl alcohol is $[\alpha]_D$ −23·0°. The ratio between these figures, namely, 1:1·47, agrees closely with that given for the similar ratio for hyoscyamine (Carr and Reynolds, Trans., 1910, **97**, 1328), namely, 1:1·48.

Like hyoscyamine, nor-hyoscyamine is converted by the action of dilute alkalis into its racemic modification, nor-atropine, which differs in many of its properties from nor-hyoscyamine. *Nor-atropine*, $C_{16}H_{21}O_3N$, is a white, crystalline base melting at 113—114°; it forms a monohydrate melting at 73°, which solidifies after drying at 100° and then melts at 113—114°. Nor-atropine forms well-crystallised salts, of which the following have been characterised: *hydrochloride*, $C_{16}H_{21}O_3N,HCl$; *sulphate*,

$$(C_{16}H_{21}O_3N)_2,H_2SO_4;$$

oxalate, $(C_{16}H_{21}O_3N)_2,H_2C_2O_4$; *aurichloride*, $C_{16}H_{21}O_3N,HAuCl_4$; and *picrate*.

Nor-atropine was methylated by treatment with methyl iodide, and the resulting methyl compound was shown to be identical with natural atropine.

Physiological Properties.

The close chemical relationship of nor-hyoscyamine and nor-atropine to hyoscyamine and atropine lends much interest to the relationship of their physiological properties. Dr. P. P. Laidlaw, of the Wellcome Physiological Research Laboratories, to whom the authors wish to express their best thanks, has kindly made comparative tests of the mydriatic effect produced by instilling solutions of the alkaloids into cats' eyes.

According to preliminary tests, nor-hyoscyamine is approximately one-eighth as active as *l*-hyoscyamine, and therefore about one-fourth as active as atropine.

Nor-atropine is, again, about one-eighth as active as atropine and one-half as active as nor-hyoscyamine; thus the ratio of the mydriatic activity of nor-hyoscyamine to that of nor-atropine is the same as that between *l*-hyoscyamine and atropine, namely, two to one.

Comparative tests as to the action on the vagus nerve are being carried out. It is also the authors' intention to prepare the *N*-ethyl and *N*-propyl derivatives, and to have their activity determined.

Hydrolysis.

When hydrolysed by the action of dilute barium hydroxide, nor-hyoscyamine and nor-atropine both give tropic acid and the volatile alkaloid nortropanol, according to the equation:

$$C_{16}H_{21}O_3N + H_2O = C_9H_{10}O_3 + C_7H_{13}ON.$$

Nortropanol has been previously described by Merling (*Annalen*, 1883, **216**, 343), who obtained it by oxidising tropine with potassium permanganate in alkaline solution.

In addition to nortropanol, another base, melting at 206°, is produced in very small amount during the hydrolysis. This base, which is crystalline, is readily soluble in water, and forms crystalline salts. Analysis has given figures agreeing with the formula $C_{12}H_{17}O_2N$. Owing to the small quantity available, this substance awaits further investigation.

Reactions.

Like the other alkaloids of this group, nor-hyoscyamine and nor-atropine give an intense, reddish-violet coloration when a small amount is heated on a watch-glass with a few drops of nitric acid, alcoholic potassium hydroxide being subsequently added (Vitali reaction). They also give crystalline precipitates when a solution of bromine in hydrobromic acid is added to a dilute solution of a salt (Wormley test). When the alkaloids are pure the best means of distinguishing them from other mydriatic alkaloids and from each other is by the solubility of their oxalates and by the melting points of the bases and their various salts tabulated below.

The picrates of the mydriatic alkaloids are of particular service in identifying the latter. They are sparingly soluble in water, and differ markedly in their melting points. For this reason the melting points of the picrates of nor-hyoscyamine and nor-atropine have been taken, and those of the other mydriatic alkaloids re-determined:

Comparison of the Melting Points of the Mydriatic Alkaloids and their Chief Salts.

	Hyoscyamine.	Atropine.	Nor-hyoscyamine.	Nor-atropine.	*l*-Hyoscine.	*i*-Scopolamine.
Alkaloid	107°	116—117°	140·5°	113—114°	—	—
Hydrochloride	—	163	207	193	200°	—
Sulphate	205—209	194	249	257	—	—
Oxalate	176	196—197	245	247—248	—	—
Aurichloride	165	137—139	178—179	157	198—200	208°
Picrate	165—166	175—176	220	227	180—181	193

Occurrence in Other Plants.

Nor-hyoscyamine has been found to occur in *Datura metel.* The alkaloids of this plant have already been described by Schmidt (*Arch. Pharm.*, 1905, **243**, 309), who does not, however, appear to have found nor-hyoscyamine in it. Working with a large quantity of the dried plant, consisting of root, stem, and leaf, the authors have obtained in pure condition:

0·01 per cent. of nor-hyoscyamine.
0·04 „ „ hyoscyamine.
0·10 „ „ hyoscine.

The alkaloids of the allied species of *Datura meteloides* have been described by Pyman and Reynolds (Trans., 1908, **93**, 2077), who also did not observe the presence of nor-hyoscyamine. The present authors, however, have obtained from a large quantity of the dried plant, consisting of root, stem, and leaf:

0·02 per cent. of nor-hyoscyamine.
0·03 „ „ atropine.
0·10 „ „ hyoscine.
0·05 „ „ meteloidine.

Lastly, nor-hyoscyamine has been found in *Duboisia myoporoides*, the dried leaf and stem of which have yielded:

0·15 per cent. of nor-hyoscyamine, and
1·1 „ „ hyoscyamine.

In 1893, E. Merck (*Arch. Pharm.*, **231**, 117) investigated the alkaloids of this plant, and isolated from them a base which he called ψ-hyoscyamine. This was stated to be an isomeride of hyoscyamine. The properties of the substance described, however, leave little room for doubt that the alkaloid in his hands was nor-hyoscyamine, probably contaminated with a little hyoscyamine, the complete removal of which is difficult to accomplish.

The properties of Merck's alkaloid and of its salts are set out below in tabular form, side by side with those of nor-hyoscyamine. The consideration of these figures shows clearly the identity of the substances:

	ψ-Hyoscyamine.	Nor-hyoscyamine.
$[\alpha]_D$	− 21·15°	− 23°
Melting point	133—134°	140·5°
,, ,, of aurichloride	176°	178—179°
,, ,, of platinichloride.	116—150°	132—141°
,, ,, of picrate	220°	220°

Further, some of the analytical figures given by Merck do not accord well with his formula.

Thus the percentage of carbon and hydrogen found by him in the purest sample of alkaloid was: $C = 70·0$, $H = 8·2$, the calculated figures being:

$C_{16}H_{21}O_3N$ $C = 69·8$; $H = 7·6$ per cent.
$C_{17}H_{23}O_3N$ $C = 70·6$; $H = 8·0$,, ,,

The carbon and hydrogen figures obtained by the analysis of the aurichloride, however, although not very concordent among themselves, agree better for the formula adopted by Merck; yet the percentage of gold agrees well with the formula now proposed. These figures are:

$C = 31·75$, $32·00$, $32·48$, $32·22$; $H = 3·92$, $3·84$, $4·23$, $4·07$; $Au = 32·20$, $31·9$, $32·0$, $31·5$, $31·8$, $31·9$.

$C_{16}H_{21}O_3N,HAuCl_4$ requires $C = 31·26$; $H = 3·58$; $Au = 32·0$ per cent.
$C_{17}H_{23}O_3N,HAuCl_4$,, $C = 32·43$; $H = 3·81$; $Au = 31·3$,, ,,

It must therefore be concluded that the alkaloid ψ-hyoscyamine, descriptions of which have found their way into works of reference and text-books, is not an individual substance, but consists of impure nor-hyoscyamine. The use of the term ψ-hyoscyamine should consequently be discontinued.

The authors obtained in some previous work a small amount of an oxalate, melting at 213°, of an alkaloid from *Datura fastuosa.* Although they have little doubt from its general properties that this was also impure nor-hyoscyamine, they are unable, owing to disposal of the material, to offer a proof of its identity.

Finally, since an alkaloid corresponding with Merck's ψ-hyoscyamine has been found in *Mandragora vernalis* or mandrake (O. Hesse, *J. pr. Chem.*, 1901, [ii], **64**, 282), it must be concluded that this plant also contains nor-hyoscyamine; thus, five different species of plants of the order Solanaceæ are known to produce nor-hyoscyamine.

Each of the plants referred to also produces hyoscyamine, the methylation of the nitrogen atom which occurs with such frequency in nature appearing in these cases to have been arrested as regards a part of the bases present.

Only one other observation appears to have been recorded of two alkaloids occurring in the same plant, differing from each other in that one contains the imino-group and the other consists of its *N*-methyl derivative, and that is the case of coniine and methylconiine, which occur together in *Conium maculatum*.

EXPERIMENTAL.

The source of the mydriatic alkaloid employed in this investigation was in the first instance the rhizome of *Scopolia japonica;* but subsequently the stem and leaf of *Datura metel*, *Datura meteloides*, and *Duboisia myoporoides*—the latter obtained from the Philippine Islands—afforded supplies of the alkaloid. In each instance the method adopted for separating the various alkaloids was substantially the same; therefore that relating to one of the sources is alone described in detail.

Isolation of Nor-hyoscyamine.

Powdered *Scopolia japonica* (102 kilos.) was extracted by continuous percolation with hot alcohol. After removing most of the alcohol, the viscid, oily extract was washed with light petroleum to remove the fats. The residue was diluted with water, filtered, rendered alkaline with an excess of ammonia solution, and repeatedly extracted with chloroform. The united chloroform extracts were concentrated to a convenient volume, and repeatedly shaken with dilute sulphuric acid until the alkaloid was removed. The aqueous extracts were next rendered alkaline with excess of ammonia, and extracted first with ether and then with chloroform. The ethereal extract contained hyoscyamine contaminated with a little nor-hyoscyamine, whilst the chloroform extract contained chiefly nor-hyoscyamine with a little hyoscyamine.

The next stage of the purification consisted in recrystallising the oxalates of the mixed alkaloids from water. That of nor-hyoscyamine, being the least soluble, was removed first; and after a long and tedious series of recrystallisations of the fractions of higher melting point, 35·6 grams of an oxalate melting at 247° were obtained.

The base was next regenerated from this oxalate, extracted with chloroform, and the chloroform extract evaporated and dried. The alkaloid was then dissolved in ether and separated from an oily residue. The ethereal extract was dried and recrystallised from acetone. It was next converted into sulphate, and crystallised by the addition of acetone to the aqueous solution. After several recrystallisations and subsequent regeneration of the alkaloid into chloroform, a base was obtained of which the melting point and specific rotatory power could not be altered by further crystallisation.

The final yield was 30 grams of nor-hyoscyamine and 155 grams of hyoscyamine.

Nor-hyoscyamine crystallises well from acetone in prismatic crystals tending to the needle form. It melts sharply at 140·5°. It is readily soluble in methyl and ethyl alcohols, ethyl acetate, or chloroform, less readily so in ether or acetone. It is sparingly soluble in cold water, more readily in hot. Five c.c. of an aqueous solution saturated at 14° gave 0·0185 gram, or 1 gram in 270 c.c.

The aqueous solution has a strongly alkaline reaction towards indicators, even towards phenolphthalein, and may readily be titrated.

1·000 gram, made up to 25 c.c. with 50 per cent. ethyl alcohol, gave α_D −1·84° in a 2-dcm. tube, whence $[\alpha]_D$ −23·0°.

The base is anhydrous:

0·1404 gave 0·3582 CO_2 and 0·0954 H_2O. C=69·6; H=7·6.
$C_{16}H_{21}O_3N$ requires C=69·8; H=7·6 per cent.

Nor-hyoscyamine hydrochloride, $C_{16}H_{21}O_3N,HCl$, crystallises from alcohol and ether in rosettes of needles melting at 207°:

0·2198 lost nil at 110° and gave 0·1010 AgCl. Cl=11·37.
$C_{16}H_{21}O_3N,HCl$ requires Cl=11·38 per cent.

Nor-hyoscyamine sulphate, $(C_{16}H_{21}O_3N)_2H_2SO_4,3H_2O$, crystallises from acetone and water in long, slender, silky needles. It melts at 249°, and is soluble in water (1 gram in 5 c.c. at 15°):

0·25 Gram, made up to 26 c.c. with water, gave α_D −0·51° in a 2-dcm. tube, whence, calculating for the basic ion, $[\alpha]_D$ −33·8°.

0·0922 lost 0·0076 at 100°. H_2O=8·2.
0·3230 gave 0·1082 $BaSO_4$. H_2SO_4=14·08.
$(C_{16}H_{21}O_3N)_2,H_2SO_4,3H_2O$ requires H_2O=7·7;
H_2SO_4=13·96 per cent.

Nor-hyoscyamine oxalate, $(C_{16}H_{21}O_3N)_2,H_2C_2O_4$, crystallises from acetone and water in beautiful, long prisms. It melts at 245—246°, and is soluble in water (1 gram in 20 c.c. at 15°).

0·467 Gram precipitated with calcium chloride, the washed precipitate dissolved in dilute sulphuric acid, and titrated with permanganate required 14·6 c.c. $N/10$-$KMnO_4$. $H_2C_2O_4$= 14·08:

0·1561 gave 0·3629 CO_2 and 0·0998 H_2O. C = 63·4; H = 7·1.
0·1600 „ 0·3745 CO_2 „ 0·0980 H_2O. C = 63·8; H = 6·8.
$(C_{16}H_{21}O_3N)_2,H_2C_2O_4$ requires C = 63·75; H = 6·87;
$H_2C_2O_4$ = 14·06 per cent.

Nor-hyoscyamine aurichloride, $C_{16}H_{21}O_3N,HAuCl_4$, crystallises from alcohol and water in glistening, golden-yellow scales, which melt at 178—179°, and are anhydrous:

0·2075 gave 0·0667 Au. Au = 32·14.
$C_{16}H_{21}O_3N,HAuCl_4$ requires Au = 32·06 per cent.

Nor-hyoscyamine platinichloride, $(C_{16}H_{21}O_3N)_2,H_2PtCl_6,3H_2O$, crystallises from hot water in handsome, reddish-yellow prisms. It does not melt at any definite point, but commences to sinter at 132°, and is in a pasty condition at 141°:

0·1980 lost 0·0098 at 110°, and gave Pt = 0·0379; H_2O = 4·95; Pt = 19·1.
$C_{16}H_{31}O_3N,H_2PtCl_6,3H_2O$ requires H_2O = 5·3; Pt = 19·2 per cent.

Constitution of Nor-hyoscyamine.

From 0·359 gram of the alkaloid no methyl iodide was produced by the Herzig and Meyer method even at 310°, whilst a control experiment using atropine gave the theoretical quantity at 276°. Nor-hyoscyamine therefore does not contain either an *N*-CH_3 or an *O*-CH_3 grouping.

A nitrosoamine soluble in ether was obtained by acting on 0·1 gram of nor-hyoscyamine with 0·2 gram of sodium nitrite and 1·5 c.c. of 2*N*-sulphuric acid; the ethereal solution, after being thoroughly washed, gave a characteristic bluish-green colour with Liebermann's reagent. Nor-hyoscyamine therefore possesses an :NH-grouping.

Synthesis of Hyoscyamine from Nor-hyoscyamine.

Four grams of pure nor-hyoscyamine were dissolved in 8 c.c. of methyl alcohol, and 1·4 c.c. of methyl iodide were added. The mixture was allowed to remain at the room temperature for one and a-half hours, and then warmed on a water-bath. The alkaloid was regenerated, dissolved in chloroform, and the oxalate prepared. By recrystallising this salt, 1·9 grams of hyoscyamine oxalate (m. p. 176°) were obtained, and from it the alkaloid (m. p. 102°), the aurichloride (m. p. 163°), and the picrate (m. p. 164°) were produced. The melting points and general properties of the base and its salts conclusively proved it to be hyoscyamine.

A small amount of the quaternary iodide was produced at the same time.

Racemisation of Nor-hyoscyamine to Nor-atropine.

Sodium hydroxide effects the racemisation of nor-hyoscyamine, but at the same time induces partial hydrolysis. The latter occurs at such a rate that the process of racemisation may be arrested owing to the neutralisation of the alkali hydroxide if insufficient is employed; thus, in one experiment, using a 4 per cent. solution of the alkaloid in 90 per cent. alcohol, one molecular proportion of sodium hydroxide, acting on seven molecular proportions of nor-hyoscyamine, only reduced the nor-hyoscyamine to one-fourth of the original amount after twenty-one hours. No further reduction of the rotatory power took place on keeping, but a second addition of one molecular proportion of sodium hydroxide rapidly completed the conversion.

The method of preparing the racemic base, nor-atropine, is illustrated by the following experiment:

5·2 Grams of pure nor-hyoscyamine were dissolved in 52 c.c. of 95 per cent. alcohol, 0·416 gram of sodium hydroxide was added, and the solution allowed to remain for sixteen hours, when, after filtering from a crystalline deposit, it showed no optical activity. The crystalline deposit (0·66 gram) was identified as sodium tropate (m. p. of acid, 117—118°). This amount of sodium tropate indicates the hydrolysis of at least 1 gram of the original base. The filtered solution was neutralised, the alcohol removed, and the alkaloid liberated, and extracted first with ether and then with chloroform. The dried chloroform extract yielded an alkaloid, which on recrystallising from dry acetone melted at 113° and showed no optical activity.

Further quantities of nor-atropine were yielded by the mother liquors obtained during the recrystallisations of the salts of nor-hyoscyamine. The purification may be effected by crystallising from water the oxalate and the sulphate, either of which is much less soluble than the corresponding salt of nor-hyoscyamine. This nor-atropine may have occurred as such in the plant, but presumably it was to a large extent, if not entirely, formed from nor-hyoscyamine during the processes of separation and purification.

Nor-atropine, $C_{16}H_{21}O_3N$, crystallises from anhydrous acetone and ether, is readily soluble in alcohol, ethyl acetate, or chloroform, and less readily so in ether, acetone, or water. It melts at 113—114°, and readily combines with water, forming a monohydrate melting at 73°. It is optically inactive:

0·3033 Gram of hydrated base lost 0·0185 gram at 60—100°. $H_2O = 6·1$.

$C_{16}H_{21}O_3N,H_2O$ requires $H_2O = 6·1$ per cent.

0·1248 * gave 0·3228 CO_2 and 0·0858 H_2O. C = 70·6; H = 7·7.

$C_{16}H_{21}O_3N$ requires C = 69·8; H = 7·6 per cent.

Nor-atropine hydrochloride, $C_{16}H_{21}O_3N,HCl$, crystallises from absolute alcohol and acetone in slender, silky filaments melting at 193°. This salt is extremely soluble in water, and is inclined to deliquesce in the air. It is very soluble in alcohol, and almost insoluble in acetone or ether. It does not contain water of crystallisation:

0·1408 gave 0·3160 CO_2 and 0·0902 H_2O. C = 61·2; H = 7·2.
0·1352 „ 0·3040 CO_2 „ 0·0870 H_2O. C = 61·3; H = 7·2.

$C_{16}H_{21}O_3N,HCl$ requires C = 61·6; H = 7·1 per cent.

Nor-atropine sulphate, $(C_{16}H_{21}O_3N)_2,H_2SO_4$, crystallises from water in long needles melting at 257°. It is soluble in water (1 gram in 9·5 c.c.) or alcohol, and almost insoluble in acetone:

0·5200 lost nil at 120°, and gave 0·187 $BaSO_4$. $H_2SO_4 = 15·12$.

$(C_{16}H_{21}O_3N)_2,H_2SO_4$ requires $H_2SO_4 = 15·1$ per cent.

Nor-atropine oxalate, $(C_{16}H_{21}O_3N)_2,H_2C_2O_4$, may best be crystallised from hot water, when it melts at 247—248°. Its solubility in water is 1 gram in 130 c.c. at 15°, or less than one-sixth that of nor-hyoscyamine oxalate.

Nor-atropine aurichloride, $C_{16}H_{21}O_3N,HAuCl_4$, crystallises in dull rosettes of opaque, yellow leaflets, melting under hot water and crystallising on cooling. It is readily soluble in alcohol, but less so in water, and may best be crystallised from dilute alcohol, when it melts at 157°:

0·1190 gave 0·0627 Au. Au = 31·5.

$C_{16}H_{21}O_3N,HAuCl_4$ requires Au = 32·06 per cent.

Synthesis of Atropine from Nor-atropine.

4·17 Grams of pure nor-atropine were dissolved in 8 c.c. of methyl alcohol, 1·5 c.c. of methyl iodide added, and the solution was allowed to remain at the room temperature for one and a-half hours. The mixture was then warmed on a water-bath, the solvent removed, and the bases regenerated and dissolved in chloroform. The alkaloid was purified by recrystallising the oxalate from water, the more soluble later fractions giving 1·4 grams of atropine oxalate (m. p. 195°). The melting point and appearance of the aurichloride

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* Anhydrous base.

(m. p. 136—137°) and the picrate (m. p. 175°) conclusively identified it as atropine.

A small amount of the methiodide (m. p. 171°) was also produced.

Hydrolysis of Nor-hyoscyamine.

Twenty grams of nor-hyoscyamine were hydrolysed with barium hydroxide by the method usually employed for the preparation of tropine from hyoscyamine or atropine. After the addition of an excess of sulphuric acid and removal of the barium sulphate, the acid product of the hydrolysis, consisting of tropic acid (7·5 grams), was shaken into chloroform. After one crystallisation this tropic acid melted at 119°, which figure was not changed on further crystallisation. To the residual liquors barium hydroxide was added until no further barium sulphate was formed; they were then concentrated and dissolved in alcohol, and acetone was added, at which point there separated 1·4 grams of a crystalline base melting at 206° and soluble in water. The formation of this substance, which is not yet explained, has since been confirmed by repetitions of this experiment.

The alcohol and acetone were removed from the remaining liquor, and the residue was distilled under the ordinary pressure. A colourless, crystalline base melting at 161° and boiling at 233° was thus obtained. This was pure nortropanol.

Nortropanol sublimes readily at 100°:

0·1002 gave 0·2442 CO_2 and 0·0944 H_2O. C = 66·5; H = 10·5.

$C_7H_{13}ON$ requires C = 66·1; H = 10·2 per cent.

Nortropanol Aurichloride.—The identity of the base was further established by the preparation of the aurichloride, which crystallised in long, acicular crystals melting at 217°.

Nortropanol tropate crystallises readily from water, in which it is freely soluble, and melts at 165°.

Identification of Mydriatic Alkaloids by means of the Picrates.

Since the properties of the picrates of the mydriatic alkaloids afford a useful means of identifying them, the melting points of picrates of all the naturally occurring tropeines and scopoleines have been determined and revised.

The picrates were prepared by adding a cold saturated aqueous solution of picric acid to an aqueous solution of the salt, warming and cooling. They were recrystallised from alcohol and water. When attempting to identify a mydriatic alkaloid by means of the picrate, the latter, being very sparingly soluble in cold water, may be almost quantitatively removed by filtration by the aid of the pump.

0·001 Gram of an alkaloid will afford enough of its picrate for identification.

The melting points and crystalline forms are as follows:

Hyoscyamine picrate	165—166°	Rectangular plates.
Atropine picrate	175—176	Glistening scales or rectangular plates
Nor-hyoscyamine picrate	220°	Needles
Nor-atropine picrate	227	,,
l-Hyoscine picrate	180—181°	Slender, matted needles
Scopolamine ,, (*i*-hyoscine)	193	,, ,, ,,

WELLCOME CHEMICAL WORKS,
DARTFORD.

XCVIII.—*The Monohalogen Derivatives of Acenaphthene.*

By HOLLAND CROMPTON and MAGGIE WALKER.

BROMOACENAPHTHENE was first obtained by Blumenthal (*Ber.*, 1874, **7**, 1095) by the direct action of bromine on acenaphthene in ethereal solution. Its constitution was determined by Graebe (*Annalen*, 1903, **327**, 77), the bromine being in the position 3 if the system of numbering given in Richter's *Lexikon* (third edition) is employed. Chloro- and iodo-acenaphthene were prepared by one of us working with Mrs. E. R. Cyriax and Miss M. K. Harrison (Proc., 1908, **24**, 241, and 1910, **26**, 226). They are both formed by the direct action of the halogen on acenaphthene, in the case of iodine in the presence of yellow mercuric oxide. Sachs and Mosebach (*Ber.*, 1910, **43**, 2474) also obtained a chloro- and iodo-acenaphthene from 3-aminoacenaphthene by the diazo-reaction, the constitution of these compounds being thus known. We have repeated the preparation of these compounds in this way, and have found that when thus produced they are identical in all respects with those formed by the direct action of the halogen on the hydrocarbon. There is therefore no doubt that in each case the halogen is in the position 3.

These compounds being of similar constitution, and simple methods having been devised for preparing them in a pure condition, it was thought wise to submit them to a somewhat closer comparative study than they had yet obtained. The melting points, boiling points, and densities in the liquid state have therefore been carefully determined. Chloro- and bromo-acenaphthene were found to form isomorphous mixtures, with freezing points intermediate between those of the pure compounds. In order to see whether there was a similar behaviour in other cases, the freezing points of other mixtures of the halogen compounds with one another and also with acenaphthene have been determined.

Temperatures were determined throughout with short normal thermometers of Jena glass, divided into 0·1°, and, as care was taken that no part of the stem should be exposed, they are all corrected temperatures. The freezing points of the mixtures examined were determined in an apparatus similar to that of Beckmann, the tube containing the mixture being placed in a somewhat wider tube, acting as air-jacket, and this in a large beaker of water, kept at a temperature about one degree lower than that at which the mixture freezes. The densities were determined by means of a graduated pipette of the form devised by one of us, and described in Spencer's "Physical Chemistry" (Vol. I., p. 66).

3-*Chloroacenaphthene*, $C_{12}H_9Cl$.

This compound is readily formed by the action of chlorine on acenaphthene dissolved in chloroform, the chloroacenaphthene being separated from the reaction product by distillation, as previously described (Crompton and Cyriax, *loc. cit.*). A more convenient chlorinating agent has been obtained in sulphuryl chloride, and we have found the following to be the best method of preparation:

Acenaphthene is dissolved in the requisite quantity of cold chloroform, and the calculated amount (1 mol.) of sulphuryl chloride is added. A slow action sets in at once, and the mixture is allowed to remain for at least two days at the temperature of the room. The chloroform is then distilled off, and from the semisolid residue the chloroacenaphthene may be extracted by boiling it with alcohol. It is better, however, to distil the residue in order to remove any unchanged acenaphthene which may be present. On distillation rather more than two-thirds passes over at 305—310° (uncorr.). This yields on cooling a pale yellow, crystalline mass melting at about 66°, and is almost pure chloroacenaphthene. It is difficult to purify completely by crystallisation, and the most effective method of treatment was found to be to convert the compound into its very stable picrate, to crystallise this several times from alcohol, and then to wash out the picric acid with very dilute aqueous ammonia.

Chloroacenaphthene when pure crystallises in perfectly colourless leaflets or plates. An analysis of the compound was made by the Dennstedt method, in which carbon, hydrogen, and chlorine were determined simultaneously. (Found, C=76·45; H=4·93; Cl=18·70. Calc., C=76·41; H=4·78; Cl=18·81 per cent.)

The melting point determined in a capillary tube in the ordinary way is about 70·5°, but when the thermometer is immersed in the liquid it remains at 69·8° during solidification. The boiling point is 319·2°/770·5 mm.

Two sets of density determinations were carried out in different pipettes, each of about 5 c.c. capacity, at temperatures near the melting point. The following values were obtained for D_4^t:

	(I.)			(II.)	
t =	69·8°	70·6°	75·4°	69·8°	71·0°
D =	1·1954	1·1939	1·1907	1·1957	1·1937

From these determinations it appears that liquid chloroacenaphthene has the density 1·1955 at the melting point 69·8°.

Chloroacenaphthene forms a very stable *picrate*, which can be repeatedly crystallised from alcohol without decomposition. It melts at 137°. Analysis of this compound shows that it contains its two constituents in equimolecular proportion.

It has been already pointed out that chloro- and bromo-acenaphthene form isomorphous mixtures. This is indicated by the fact that the addition of chloro- to bromo-acenaphthene does not depress the freezing point, 51·2°, of the latter, but the freezing points of mixtures of the two compounds lie on a continuous curve between those of the pure substances. Determinations of the freezing points of a number of mixtures have been made, and are contained in the following table. The first column gives the molecular percentage of chloroacenaphthene present in each mixture, the second the observed freezing point, and the third the freezing point calculated on the assumption that the freezing points of the mixtures when plotted against molecular percentages lie on the straight line connecting the freezing points of the two components. In the fourth column are the differences between the calculated and the observed freezing points.

Freezing Points of Mixtures of Chloro- and Bromo-acenaphthene.

Mol. per cent. of chloroacenaphthene.	F. p. observed.	F. p. calculated.	Difference, calc.—obs.
100·00	69·8°	—	—
92·14	68·2	68·3°	0·1°
84·07	66·6	66·8	0·2
73·89	64·6	64·9	0·3
65·96	63·0	63·5	0·5
54·47	61·2	61·3	0·1
43·65	58·8	59·3	0·5
29·96	56·4	56·8	0·4
19·41	54·4	54·8	0·4
11·69	53·0	53·4	0·4
0·00	51·2	—	—

It will be seen that the observed freezing points are throughout slightly lower than the calculated. The behaviour of these mixtures therefore resembles that of some other mixtures of isomorphous substances.

The freezing points of mixtures of chloroacenaphthene with acenaphthene and also with iodoacenaphthene were determined. In these cases the freezing-point curves are of the usual form, and there is no indication of the formation of isomorphous mixtures. The results are contained in the following tables:

Freezing Points of Mixtures of Acenaphthene and Chloroacenaphthene.

Mol. per cent. of chloroacenaphthene.	F. p.	Mol. per cent. of chloroacenaphthene.	F. p.
100·00	69·8°	46·10	60·2°
91·54	66·9	42·65	63·9
82·40	63·8	32·93	71·3
73·08	61·1	24·83	76·8
64·51	58·9	17·91	81·5
61·72	58·3	9·99	86·4
55·53	57·4	0·00	92·1
50·28	57·0		

The eutectic mixture, according to these results, would contain a molecular percentage of 50·5 of chloroacenaphthene, and its melting point would be 56·6°.

Freezing Points of Mixtures of Chloro- and Iodo-acenaphthene.

Mol. per cent. of chloroacenaphthene.	F. p.	Mol. per cent. of chloroacenaphthene.	F. p.
100·00	69·8°	48·10	36·6°
93·22	65·8	42·56	33·2
86·17	61·2	38·17	33·8
80·23	57·6	31·06	40·3
74·30	53·8	23·10	46·1
63·57	46·4	13·06	52·9
57·68	43·3	0·00	62·0
53·38	40·0		

The eutectic mixture would contain a molecular percentage of 40·1 of chloroacenaphthene, and would melt at 31·8°.

3-*Bromoacenaphthene*, $C_{12}H_9Br$.

This compound is best prepared by the action of bromine dissolved in ether on acenaphthene, also in ethereal solution. The ether is distilled off, and bromoacenaphthene may be obtained from the product by extraction with alcohol. In this case, as with chloroacenaphthene, it is best to distil in order to remove unchanged acenaphthene. The greater part of the product distils at 325—330° (uncorr.), and this, although slightly brown in colour, is nearly pure bromoacenaphthene, and has a melting point of 51°. It may be purified by crystallisation from alcohol.

Bromoacenaphthene crystallises in colourless leaflets or plates, and is perfectly similar to chloroacenaphthene in appearance. The melting point in a capillary tube is a little above 52°, but a thermometer immersed in the liquid remains at 51·2° during solidification. The boiling point is 336·4°/760·5 mm.

Two sets of density determinations were made near the melting point, using the same pipettes that were employed in the case of chloroacenaphthene. The results obtained for D^t_4 were:

	(I.)			(II.)	
t =	51·4°	54·8°	55·0°	51·4°	52·4°
D =	1·4397	1·4364	1·4365	1·4392	1·4388

Calculated from these determinations, the density of liquid bromoacenaphthene is 1·4397 at the melting point 51·2°.

As chloroacenaphthene does not form isomorphous mixtures with acenaphthene or iodoacenaphthene, it was not to be expected that bromoacenaphthene would do so. The freezing points of mixtures of bromoacenaphthene with acenaphthene and iodoacenaphthene are, in fact, of the normal type. The following determinations were made:

Freezing Points of Mixtures of Acenaphthene and Bromoacenaphthene.

Mol. per cent. of bromoacenaphthene.	F. p.	Mol. per cent. of bromoacenaphthene.	F. p.
100·00	51·2°	39·00	67·6
89·82	48·5	33·82	71·3
80·65	45·6	28·47	75·1
72·47	43·2	25·79	76·7
65·47	42·0	20·10	80·6
58·94	48·6	14·44	83·9
46·29	61·3	7·90	87·6
42·47	64·4	0·00	92·1

The eutectic mixture would contain the molecular percentage 65·8 of bromoacenaphthene, and would melt at 41·5°.

Freezing Points of Mixtures of Bromo- and Iodo-acenaphthene.

Mol. per cent. of bromoacenaphthene.	F. p.	Mol. per cent. of bromoacenaphthene.	F. p.
100·00	51·2°	50·09	35·9°
91·74	48·2	46·36	38·4
82·77	44·4	33·66	45·4
75·65	41·4	26·67	49·2
71·01	39·6	19·40	52·8
63·70	36·4	10·77	56·6
56·63	33·4	0·00	62·0

The eutectic mixture would contain the molecular percentage 55·1 of bromoacenaphthene, and would melt at 32·5°.

Bromoacenaphthene combines with picric acid in equimolecular proportion to form a picrate melting at 114°. This is less stable than the picrate of chloroacenaphthene, and decomposes gradually on repeated crystallisation from alcohol.

3-*Iodoacenaphthene*, $C_{12}H_9I$.

Iodoacenaphthene is readily obtained by treating acenaphthene, in solution in methyl or ethyl alcohol, with iodine in the presence of yellow mercuric oxide. Acenaphthene is dissolved in the hot alcohol, rather more than the calculated amount of mercuric oxide is added, and then the iodine is gradually introduced, the liquid being well shaken during this operation. The solution is finally raised to the boiling point, and filtered. Iodoacenaphthene crystallises out on cooling, mixed with some mercuric iodide. The crude product is treated with cold chloroform, in which iodoacenaphthene is extremely soluble, and the mercuric iodide removed by filtration. The chloroform is distilled off, and the residue is purified by crystallisation from alcohol. It has been found advantageous in purifying iodoacenaphthene to convert it into the picrate, to crystallise this from alcohol, and then to remove the picric acid with aqueous ammonia.

It was analysed by the Dennstedt method. (Found, C = 50·94; H = 3·35; I = 45·43. Calc., C = 51·43; H = 3·21; I = 45·36 per cent.)

Iodoacenaphthene crystallises in colourless needles or prisms, very different in appearance from the chloro- or bromo-compound. It melts in a capillary tube at a little above 65°, but when a thermometer is immersed in the liquid, supercooling takes place to a considerable extent, and during solidification the temperature does not rise above 62°. Repeated fusion lowers the melting point still further, and the liquid appears to undergo some slight decomposition. Iodoacenaphthene decomposes completely when strongly heated, with copious liberation of iodine, the temperature at which this sets in varying somewhat with the mode of heating, but being usually about 180°.

Two sets of density determinations, similar to those carried out in the previous cases, were made with this compound. The values obtained for D^t_4 are as follows:

	(I.)			(II.)		
t =	63·2°	65·0°	66·8°	63·8°	65·1°	66·8°
D =	1·6727	1·6708	1·6689	1·6717	1·6705	1·6684

The density of liquid iodoacenaphthene calculated from these determinations at the melting point 62° is 1·6738.

Iodoacenaphthene forms with picric acid in equimolecular proportion an orange-red picrate melting at 102·5°. This is a somewhat unstable compound, and is entirely decomposed by two or three crystallisations from alcohol.

The freezing points of mixtures of iodoacenaphthene with acenaphthene itself have been determined. There is no sign of the production of mixed crystals, and the freezing-point curve is therefore of the usual type. The results obtained are given in the following table:

Freezing Points of Mixtures of Acenaphthene and Iodoacenaphthene.

Mol. per cent. of iodoacenaphthene.	F. p.
100·00	62·0°
86·94	52·6
76·89	44·8
71·39	40·6
66·61	38·7
60·43	47·6
58·84	50·2
53·35	55·2
44·00	63·6
39·51	67·3°
34·33	71·1
28·23	75·6
27·03	76·3
21·48	79·8
15·07	83·8
7·58	88·2
0·00	92·1

The eutectic mixture would contain a molecular percentage of 67·2 of iodoacenaphthene, and would melt at 37·6°.

It is obvious that the formation of mixed crystals occurs to any marked extent with mixtures of chloro- and bromo-acenaphthene only. The molecular volumes of the compounds here dealt with at the melting points have the following values:

Acenaphthene	150·61
Chloroacenaphthene ...	157·67
Bromoacenaphthene ...	161·84
Iodoacenaphthene ...	167·28

It will be seen that the molecular volumes differ least from one another in the case of chloro- and bromo-acenaphthene. This may be connected with the formation of mixed crystals by these compounds only.

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XCIX.—*The Molecular Conductivities of Potassium Nitrite, Mercuric Nitrite, and Potassium Mercurinitrite.*

By PRAFULLA CHANDRA RÂY and NILRATAN DHAR.

IT is generally assumed that a solution of potassium mercurinitrite, $K_2Hg(NO_2)_4$, contains mercury, not as a cation, but as a part of a complex bivalent anion, $Hg(NO_2)_4''$. In support of this view it is urged that whereas mercuric nitrate on dilution undergoes hydrolysis with the formation of the characteristic basic salts, the former salt "can be dissolved in water without any sign of decomposition" (compare Ostwald's "Principles of Inorganic Chemistry," Findlay's translation, 1908, pp. 673 and 683).

The ionisation of the nitrites and the so-called double nitrites as measured by the cryoscopic method (Proc., 1910, **26**, 173) threw doubt on the correctness of the above assumption. It therefore seemed desirable to measure the molecular conductivities of potassium mercurinitrite as also of its components.

Preparation of Potassium Nitrite, Mercuric Nitrite, and Potassium Mercurinitrite.—One of us has already shown that solutions of the alkali nitrites can safely be evaporated on a water-bath (Trans., 1905, **87**, 178). It has since then been discovered that the alkali nitrites thus prepared are not absolutely pure, as the solutions at 100°, and even at lower temperatures, undergo hydrolysis, although to a very slight extent; thus, when solutions of calcium and strontium nitrites are evaporated, thin pellicles of their carbonates are formed on the surface.

The following modified method was therefore adopted. The solutions of barium nitrite and potassium sulphate (both purified by recrystallisation) were mixed in equivalent proportions, and the precipitate of barium sulphate was allowed to settle for a day or two in a stoppered cylinder. The clear liquid was withdrawn by means of a pipette, and if particles of barium sulphate remained in suspension they were removed by filtration.* The filtrate was evaporated in a vacuum desiccator over sulphuric acid nearly to dryness, and the crystals of potassium nitrite were freed from adhering mother liquor by being pressed through folds of filter paper.†

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* This procedure is necessary, as barium sulphate, unless rendered crystalline by boiling in a slightly acid solution, is apt to run through the filter paper.

† For the preparation of mercuric nitrite and potassium mercurinitrite, see Trans., 1904, **85**, 523, and 1907, **91**, 2031.

Molecular Conductivity of Potassium Nitrite.

Volume in litres, v.	Molecular conductivity at 20°, μ.
8·5	95·00
25·5	110·51
76·5	120·12
229·5	132·13
688·5	136·03
2065·5	142·02

*Molecular Conductivity of Mercuric Nitrite.**

Volume in litres, v.	Molecular conductivity at 20°, μ.
17	5·16
51	7·00
153	10·18
459	14·13
1377	34·51
4131	83·32

* Ley and Kissel's measurement of electrical conductivity gives $\mu_{32}=6·2$, $\mu_{64}=8·6$, $\mu_{128}=12·7$ (*Ber.*, 1899, **32**, 1363). Our measurements were made of a solution of crystals of mercuric nitrite, whereas the above-named workers evidently used the ordinary solution prepared by double decomposition between mercuric chloride and silver nitrite.

Molecular Conductivity of Potassium Mercurinitrite.

Volume in litres, v.	Molecular conductivity at 20°, μ.
17	180·80
51	218·00
153	242·11
459	271·60
1377	300·00
4131	362·15

A comparison of the molecular conductivity of potassium mercurinitrite with the molecular conductivities of its constituents is given below:

$Hg(NO_2)_2$.		$2KNO_2$.		Sum	$2KNO_2,Hg(NO_2)_2$.		
v.	μ.	v.	μ.	(calc.).	v.	μ.	Difference.
17	5·16	8·5	190·00	195·16	17	180·80	14·36
51	7·00	25·5	221·02	228·02	51	218·00	10·02
153	10·18	76·5	240·24	250·42	153	242·11	8·31
459	14·13	229·5	264·26	278·39	459	271·60	6·79
1377	34·51	688·5	272·06	306·57	1377	300·00	6·57
4131	83·32	2065·5	284·02	367·34	4131	362·15	5·21

The molecular conductivity of mercuric nitrite is taken at the same volume as potassium mercurinitrite; that of potassium nitrite is taken as twice the molecular conductivity of potassium nitrite at one-half the volume of potassium mercurinitrite. From the foregoing comparison it is seen that very little of the complex ion, $Hg(NO_2)_4''$, mercurinitrosion, exists in solution.

The complex anion formation in this case is nearly of the same order as in the case of double chlorides (Jones and Mackay, *Amer. Chem. J.*, 1897, **19**, 83; Jones and Ota, *ibid.*, 1899, **22**, 5 and 12) (for example, ammonium mercurichloride) and double sulphates (MacGregor, *Phil. Mag.*, 1896, [v], **41**, 276; MacGregor and Archibald, *ibid.*, 1898, [v], **46**, 509) (for example, potassium cuprisulphate).

Potassium mercurinitrite, even at a dilution of 17 litres, contains sufficient dimercurion ($Hg^{\cdot\cdot}$); hence sodium hydroxide precipitates the latter as HgO, or rather $Hg(OH)_2$. Moreover, potassium nitrite has a very slightly alkaline reaction due to hydrolysis, whilst mercuric nitrite is distinctly acid; potassium mercurinitrite, on the other hand, is slightly acid towards litmus. This would not have been the case if it were a complex salt, since potassium hydroxide is a strong base. The rational explanation seems to be that the acidity of mercuric nitrite more than counterbalances the alkalinity due to the hydrolysis of potassium nitrite, and renders potassium mercurinitrite, on the whole, acid.

Sherril (*Zeitsch. physikal. Chem.*, 1903, **43**, 735) has also shown from potential difference measurements that

$$\frac{Hg(Cl)_4''}{Hg^{\cdot\cdot} \times (Cl')^4} = 1{\cdot}6 \times 10^{16},$$

whilst Hans Pick (*Diss.*, Breslau, 1906, 63) has shown that

$$\frac{Hg(NO_2)_4''}{Hg^{\cdot\cdot} \times (NO_2')^4} = 3{\cdot}5 \times 10^{13}.$$

Thus mercurinitrosion, $Hg(NO)_4''$, is nearly 500 times less stable than mercurichloridion, ($HgCl_4''$).

The fact that potassium mercurinitrite allows of the formation of a clear, bright solution is not evidently due to its containing the complex ion, $Hg(NO_2)_4''$, as interpreted by Ostwald. Mercuric nitrite itself, like mercuric chloride, is very feebly ionised in solution, and can be diluted to any extent without the formation of basic salts. It is for this reason that a solution of sodium sulphate when added to a solution of mercuric nitrate at once precipitates the basic sulphate known as turpeth mineral, whereas mercuric nitrite with the latter reagent remains unaffected.

Apart from the method of preparation of potassium mercurinitrite followed by one of us, which is of wide and general application (*loc. cit.*), two others have been described, namely, by dissolving mercuric oxide in potassium nitrite and destroying the basic reaction with acetic acid (Ostwald, *loc. cit.*), and by treating a solution of mercuric nitrate with excess of potassium nitrite (Lang, *J. pr. Chem.*, 1862, **86**, 295).

Ostwald is of opinion that it is the tendency towards the formation of the complex ion, $Hg(NO_2)_4''$, that brings about this reaction. In the light of the conductivity measurements of mercuric nitrite, it is more likely that it is the resistance of this salt to ionisation which is the determining factor in the reaction (compare the interaction of sodium acetate and hydrochloric acid in dilute solution, in which, owing to the non-ionisation of acetic acid, the latter accumulates).

Again, mercuric nitrite combines with potassium nitrite in several other proportions; thus, the following salts have already been described: $Hg(NO_2)_2 + 3KNO_2 + H_2O$; $Hg(NO_2)_2 + KNO_2$ (Trans., 1907, **91**, 2032), and $3Hg(NO_2)_2 + 2KNO_2$ (Proc., 1910, **26**, 172). The formation of the latter compounds would scarcely be expected if there were only the stable complex anion, $Hg(NO_2)_4''$, in solution.

Summary and Conclusion.—From the foregoing investigation it would appear that in potassium mercurinitrite there exists very little of the complex anion, $Hg(NO_2)_4''$. Kalion ($K^{\cdot}$), nitrosion (NO_2'), and dimercurion ($Hg^{\cdot\cdot}$), however, exist as separate entities.

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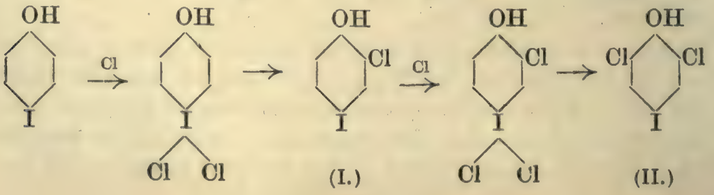
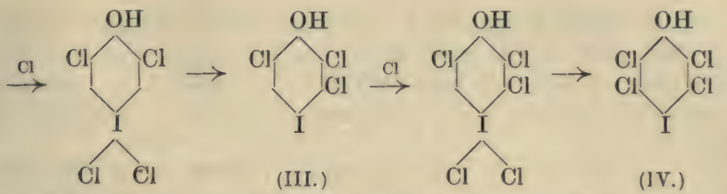
C.—*The Chlorination of Iodophenols. Part I. The Chlorination of* p-*Iodophenol.*

By Sidney Albert Brazier, M.Sc. (Priestley Research Scholar of the University of Birmingham), and Hamilton McCombie.

When an ice-cold solution of *p*-iodophenol in carbon tetrachloride is saturated with chlorine, a yellow, crystalline iodo-dichloride is precipitated. This substance is very unstable, and, in the course of a few minutes, undergoes decomposition, liberating hydrogen chloride and forming 2-chloro-4-iodophenol (I). This substance, in turn, when subjected to the action of chlorine, also yields an unstable iodo-dichloride, which decomposes to form 2 : 6-dichloro-4-iodophenol (II). On repeating the process with the latter compound, an unstable iodo-dichloride is again obtained, from which, by decomposition, 2 : 3 : 6-trichloro-4-iodophenol (III) results. This compound, on further chlorination and decomposition of the iodo-dichloride first formed, gives 2 : 3 : 5 : 6-tetrachloro-4-iodophenol (IV). The chain of reactions can be represented as follows:




(III.) (IV.)

Various decompositions of iodo-dichlorides with evolution of chlorine and hydrogen chloride have been described, but in the majority of cases these decompositions have been effected only by the action of heat.

Willgerodt (*J. pr. Chem.*, 1886, [ii], **33**, 154) describes the decomposition of iodobenzene dichloride, stating that it evolves all its chlorine at 115—120°. Later (*Ber.*, 1893, **25**, 3494), the same observer remarks that this iodo-dichloride, when exposed to moist air, decomposes with evolution of hydrogen chloride. Keppler (*Ber.*, 1898, **31**, 1136) has shown that iodobenzene dichloride when kept in sealed tubes, even in the dark, decomposes with the formation of *p*-chloroiodobenzene. Somewhat similar results have been obtained by Werner in his work on the effect of heat on various iodo-dichlorides (Trans., 1907, **91**, 529).

Willgerodt (*Ber.*, 1894, **27**, 590) and also Willgerodt and Schlösser (*Ber.*, 1900, **33**, 692) state that the iodonaphthalene dichlorides decompose on keeping, giving chlorine substituted products. Again, Willgerodt and Smith (*Ber.*, 1904, **37**, 1312) state that *p*-iodoazobenzene dichloride evolves chlorine rapidly when exposed to the air. Willgerodt and Roggatz (*J. pr. Chem.*, 1900, [ii], **61**, 424) state that iodomesitylene dichloride decomposes, even in solution, forming chloroiodomesitylene, with evolution of chlorine and hydrogen chloride.

o-Iodoanisole and *o*-iodophenetole also yield unstable iodo-dichlorides. Jannasch and Hinterkirch (*Ber.*, 1898, **31**, 1710) showed that *o*-iodoanisole dichloride, on keeping, or on adding to potassium iodide, yields 5-chloro-2-iodoanisole; *o*-iodophenetole behaves in the same way.

p-Iodoanisole and *p*-iodophenetole, the preparations of which are described by Liebrecht (D.R.-P. 161725, Abstr., 1906, i, 257), when chlorinated, are said by Mascarelli and Martinelli (*Atti R. Accad. Lincei*, 1907, [v], **16**, i, 183) to yield ring-substituted products quite easily.

Willgerodt and Simonis (*Ber.*, 1906, **39**, 276) describe the chlorination of *p*-iodoaceto-*m*-toluidide, which yields an iodo-dichloride, from which 6-chloro-4-iodoaceto-*m*-toluidide results on decomposition.

The only statement which the authors have been able to discover about the chlorination of iodophenols is one by Willgerodt (*Ber.*, 1892, **25**, 3495) to the effect that when *o*-iodophenol or 2:4:6-tri-iodophenol is treated with chlorine in chloroform solutions, compounds result in which the iodine has been displaced by chlorine.

The constitutions of the compounds formed when the iodo-dichlorides undergo decomposition were established by subjecting the first two decomposition products to the action of nitric acid. In both cases the same product resulted, and this was shown to be 6-chloro-2:4-dinitrophenol. This compound has been prepared by various observers, and its constitution is undoubted. It is produced by the action of nitric acid on *o*-chlorophenol (Griess, *Annalen*, 1859, **109**, 286; Faust and Müller, *ibid.*, 1874, **173**, 312), from *o*-nitrophenol by chlorination and subsequent nitration (Faust and Saame, *Annalen, Suppl.*, 1869–70, **7**, 195), and similarly from *p*-nitrophenol (Seifart, *ibid.*, 197).

Whilst the simple phenols yield unstable iodo-dichlorides which readily decompose, giving ring-substitution products, stable iodo-dichlorides are easily obtained from the acetyl and benzoyl derivatives of the phenols. An exception to this generalisation is *p*-iodophenyl acetate, the iodo-dichloride of which is found to decompose after having been kept for ten days. In this connexion the observation of Mascarelli and Martinelli (*loc. cit.*) as to the instability of the iodo-dichlorides derived from *p*-iodo-anisole and -phenetole, is of great interest.

When attempts were made to convert 2:3:5:6-tetrachloro-4-iodophenol into an iodo-dichloride, even if the solution was saturated with chlorine for several hours, only the unchanged compound could be obtained. This inhibitive action of the two ortho-substituents on the production of iodo-dichlorides has been commented on by Willgerodt. This experimenter noticed (*Ber.*, 1910, **43**, 2755) that tetrachloroiodobenzene could not be caused to yield an iodo-dichloride when the two positions adjacent to the iodine atom are occupied by chlorine atoms. Willgerodt and Meyer (*Annalen*, 1911, **385**, 351) noticed similar behaviour in the case of 4:6-dichloro-5-iodo-ψ-cumene.

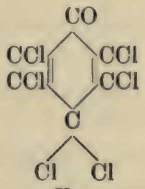
Another curious example of the influence of substituents on the course of a reaction was encountered in the preparation of the benzoyl derivatives of these phenols. Benzoylation in presence of sodium hydroxide yielded quite satisfactory results when one at least of the ortho-positions relative to the hydroxyl groups was occupied by hydrogen. This is shown in the case of the benzoylation of *p*-iodophenol and 2-chloro-4-iodophenol. When, however, both ortho-positions relative to the hydroxyl group are occupied by chlorine atoms, benzoyl chloride in presence of sodium hydroxide yielded practically no benzoyl derivative. If, however, the sodium hydroxide is replaced by pyridine, the reaction proceeds quite smoothly.

A study of the melting points of the different series of compounds described in this paper gives some interesting results.

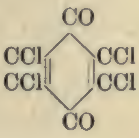
Phenol.	Benzoyl derivative.	Iodo-dichloride.	Acetyl derivative.	Iodo-dichloride.	
91°	125°	132—133°	38°	116°	*p*-iodophenol
54	72	126—127	49	123	2-chloro-4-iodophenol
91—92	62—63	125	72	126	2 : 6-dichloro-4-iodophenol
51—52	oil	133—134	82	146	trichloroiodophenol
72	110—111	—	105	—	tetrachloroiodophenol

From the accompanying table it is seen that, in the case of the phenols, the unsymmetrical compounds have lower melting points than the symmetrical ones. This is seen in the case of 2-chloro- and 2 : 3 : 6-trichloro-4-iodophenol. The benzoyl derivatives, however, do not follow this rule. In the case of the acetyl derivatives and their iodo-dichlorides, the melting points rise steadily with the introduction of each chlorine atom.

If, instead of employing an ice-cold solution of *p*-iodophenol for these chlorination experiments, chlorine is led into a solution warmed to 50—60°, the solution is found to darken with liberation of iodine, and hydrogen chloride is evolved. If the chlorination is continued until no more hydrogen chloride is given off, four different products can be isolated from the reaction mixture, namely, (1) 2 : 3 : 5 : 6-tetrachloro-4-iodophenol (IV); (2) pentachlorophenol; (3) hexachloro*cyclo*hexadienone (V); and (4) chloroanil (VI):



(V.)



(VI.)

The constitutions of all these substances were easily established. Hexachloro*cyclo*hexadienone, on treatment with potassium iodide, yielded pentachlorophenol with liberation of iodine; this reaction was easily followed quantitatively, and was found to be in agreement with the equation:

$$C_6OCl_6 + 2KI = C_6Cl_5{\cdot}OK + KCl + I_2.$$

EXPERIMENTAL.

The *p*-iodophenol used in these experiments was prepared from *p*-aminophenol by the diazo-reaction in 30 per cent. sulphuric acid (compare Noelting and Stricker, *Ber.*, 1887, **20**, 3018). The crude substance, which melted at 90—91°, was used for the chlorinations without further purification.

p-*Iodophenyl Acetate*, $C_6H_4I{\cdot}OAc$.

Willgerodt (*Ber.*, 1909, **42**, 3767) states that he was unable to obtain this compound in crystalline form. Wohlleben (*Ber.*, 1909, **42**, 4374) also describes it, and gives its melting point at 32—32·5°. We obtained it easily by the following method. Ten grams of *p*-iodophenol, mixed with 3 grams of acetic anhydride, were heated on a water-bath for a few minutes, a few drops of concentrated sulphuric acid were added, and the reaction mixture was poured into water. It crystallised from methyl alcohol in small, white leaflets melting at 38°. (Found, I=48·61. Calc., I=48·48 per cent.)

The *Iodo-dichloride*.—Willgerodt (*loc. cit.*) states that on chlorinating a solution of *p*-iodophenyl acetate, yellow crystals separated, but decomposed rapidly in the solution.

We found that on chlorinating *p*-iodophenyl acetate in carbon tetrachloride solution, small, yellow needles separated, which melted and decomposed at 116°. After remaining for several days without apparent change, the crystals decomposed rapidly with evolution of hydrogen chloride:

0·1518 gave 0·2384 AgCl + AgI.

$C_8H_7O_2Cl_2I$ requires AgCl + AgI = 0·2380.

Action of Chlorine on p-*Iodophenol. Preparation of 2-Chloro-4-iodophenol*, $C_6H_3ClI{\cdot}OH$.

Ten grams of powdered *p*-iodophenol were dissolved in 250 c.c. of carbon tetrachloride. The solution, cooled in ice, was saturated with chlorine, and fine crystals soon separated. The chlorination was continued for fifteen to twenty minutes, after which the crystals were collected. If the crystals were allowed to remain in the liquid too long, decomposition of the iodo-dichloride began. The filtered solution was again chlorinated, when a further crop of crystals was obtained. The crystals were transferred quickly to a small beaker, which was then cooled in ice. After a short time decomposition began with a violent evolution of hydrogen chloride. When decomposition was complete, the resulting product, which was very dark in colour, was exposed to a strong draught for some time, and a much paler product was obtained. A theoretical yield of the iodo-dichloride was obtained, which gave from 10 to 12 grams of the crude decomposition product. This was recrystallised from carbon tetrachloride, when it was deposited in needles melting at 54°. The substance was very soluble in methyl and ethyl alcohols, benzene, or light petroleum:

0·1329 gave 0·1962 AgCl + AgI.

C_6H_4OClI requires AgCl + AgI = 0·1976.

On treatment with concentrated nitric acid, this compound yields 6-chloro-2:4-dinitrophenol, which melts at 110—111°. This establishes the constitution.

2-*Chloro-4-iodophenyl Acetate*, $C_6H_3ClI{\cdot}OAc$.

When recrystallised twice from methyl alcohol, this substance melted at 49°. It is very soluble in alcohol or benzene, but crystallises from methyl alcohol in long, triangular prisms:

0·1931 gave 0·2451 AgCl + AgI.

$C_8H_6O_2ClI$ requires AgCl + AgI = 0·2466.

The *iodo-dichloride* is a fine, yellow powder melting and decomposing at 123°. After being kept for about ten days, it decomposed with evolution of hydrogen chloride:

0·1395 gave 0·2484 AgCl + AgI.

$C_8H_6O_2Cl_3I$ requires AgCl + AgI = 0·2526.

2-*Chloro-4-iodophenyl Benzoate*, $C_6H_3ClI{\cdot}OBz$.

This was prepared by the Schotten-Baumann reaction, a theoretical yield being obtained. The substance, crystallised twice from methyl alcohol, gave crystals melting at 72°:

0·1691 gave 0·1772 AgCl + AgI.

$C_{13}H_8O_2ClI$ requires AgCl + AgI = 0·1784.

The *iodo-dichloride* melted and decomposed at 126—127°. This substance, in contradistinction to the iodo-dichloride of the acetyl derivative, was quite stable:

0·1117 gave 0·1718 AgCl + AgI.

$C_{13}H_8O_2Cl_3I$ requires AgCl + AgI = 0·1730.

2:6-*Dichloro-4-iodophenol*, $C_6H_2Cl_2I{\cdot}OH$.

Ten grams of the crude 2-chloro-4-iodophenol were dissolved in 150 c.c. of carbon tetrachloride and chlorinated. The dichloride separated quickly in fine, yellow crystals, and, after chlorinating for fifteen to twenty minutes, the crystals were collected. Further crops of the dichloride were obtained by successive chlorinations of the filtrate. The dichloride, after filtration, rapidly decomposed, giving a dark-coloured decomposition product, which was recrystallised from a mixture of equal quantities of methylated spirit and water. After two recrystallisations, needles melting at 91—92° were obtained.

2:6-*Dichloro-4-iodophenol* is readily soluble in methyl alcohol, methylated spirit, or light petroleum:

0·1144 gave 0·2053 AgCl + AgI.

$C_6H_3OCl_2I$ requires AgCl + AgI = 0·2064.

On treatment with concentrated nitric acid this compound yields 6-chloro-2:4-dinitrophenol, which melts at 110—111°. This establishes the constitution.

2:6-*Dichloro-4-iodophenyl Acetate*, $C_6H_2Cl_2I\cdot OAc$.

This was recrystallised three times from methyl alcohol, and gave long needles melting at 72°. It is very soluble in ethyl alcohol, benzene, or light petroleum:

0·1413 gave 0·2215 AgCl + AgI.

$C_8H_5O_2Cl_2I$ requires AgCl + AgI = 0·2238.

The *iodo-dichloride* forms light, yellow crystals, melting and decomposing at 126°:

0·1201 gave 0·2394 AgCl + AgI.

$C_8H_5O_2Cl_4I$ requires AgCl + AgI = 0·2417.

2:6-*Dichloro-4-iodophenyl Benzoate*, $C_6H_2Cl_2I\cdot OBz$.

This was prepared by the method described by Einhorn and Hollandt (*Annalen*, 1898, **301**, 95).

2·8 Grams of benzoyl chloride were added gradually to a well-cooled solution of 4 grams of pure dichloroiodophenol dissolved in 40 grams of pyridine. The mixture was allowed to remain overnight, and was then poured into dilute sulphuric acid. After two days the mass became solid, and was collected and crystallised from methyl alcohol. The substance is fairly soluble in methyl alcohol, ethyl alcohol, or benzene, and forms crystals melting at 62—63°:

0·1869 gave 0·2471 AgCl + AgI.

$C_{13}H_7O_2Cl_2I$ requires AgCl + AgI = 0·2482.

The *iodo-dichloride* was obtained in stable, yellow leaflets melting and decomposing at 125°:

0·1224 gave 0·2123 AgCl + AgI.

$C_{13}H_7O_2Cl_4I$ requires AgCl + AgI = 0·2134.

2 : 3 : 6-*Trichloro-4-iodophenol*, $C_6HCl_3I{\cdot}OH$.

Five grams of pure dichloroiodophenol dissolved in 50 c.c. of carbon tetrachloride were saturated with chloride. The dichloride separated as a fine, almost amorphous powder, which rapidly decomposed after collection. The resulting product was recrystallised several times from a mixture of alcohol and water, or from light petroleum, and separated in small, white needles melting at 51—52°:

0·1158 gave 0·2357 AgCl + AgI.

$C_6H_2OCl_3I$ requires AgCl + AgI = 0·2379.

2 : 3 : 6-*Trichloro-4-iodophenyl Acetate*, $C_6HCl_3I{\cdot}OAc$.

This substance, when recrystallised three times from methyl alcohol, forms white needles melting at 82°:

0·1039 gave 0·1905 AgCl + AgI.

$C_8H_4O_2Cl_3I$ requires AgCl + AgI = 0·1891.

The *iodo-dichloride* melts and decomposes at 146°:

0·1084 gave 0·2349 AgCl + AgI.

$C_8H_4O_2Cl_5I$ requires AgCl + AgI = 0·2365.

2 : 3 : 6-*Trichloro-4-iodophenyl Benzoate*, $C_6HCl_3I{\cdot}OBz$.

This substance could not be obtained in a crystalline form.

The *iodo-dichloride* melts and decomposes at 133—134°:

0·1105 gave 0·2127 AgCl + AgI.

$C_{13}H_6O_2Cl_5I$ requires AgCl + AgI = 0·2111.

2 : 3 : 5 : 6-*Tetrachloro-4-iodophenol*, $C_6Cl_4I{\cdot}OH$.

This compound was obtained by the decomposition of the iodo-dichloride derived from trichloroiodophenol. It was, however, more easily obtained by the steam distillation of the crude product obtained on chlorinating *p*-iodophenol in warm solution. After several recrystallisations from a mixture of alcohol and water, or from light petroleum, it yielded white needles melting at 72°:

0·1064 gave 0·2418 AgCl + AgI.

C_6HOCl_4I requires AgCl + AgI = 0·2405.

All attempts to convert 2 : 3 : 5 : 6-tetrachloro-4-iodophenol into an iodo-dichloride resulted in the recovery of the unchanged substance.

2:3:5:6-*Tetrachloro-4-iodophenyl Acetate*, $C_6Cl_4I{\cdot}OAc$.

This was obtained, when recrystallised from methyl alcohol, in clusters of fine needles melting at 105°. The iodo-dichloride could not be obtained:

0·1158 gave 0·2330 AgCl + AgI.

$C_8H_3O_2Cl_4I$ requires AgCl + AgI = 0·2342.

2:3:5:6-*Tetrachloro-4-iodophenyl Benzoate*, $C_6Cl_4I{\cdot}OBz$.

On recrystallisation from methyl alcohol, this compound separated in small plates melting at 110—111°. The iodo-dichloride could not be obtained:

0·1319 gave 0·2335 AgCl + AgI.

$C_{13}H_5O_2Cl_4I$ requires AgCl + AgI = 0·2310.

Action of Chlorine on a Warm Solution of p-*Iodophenol.*

On chlorinating *p*-iodophenol in warm carbon tetrachloride solution, four different products resulted, namely, (1) 2:3:5:6-tetrachloro-4-iodophenol, (2) pentachlorophenol, (3) hexachloro*cyclo*hexadienone, and (4) chloroanil.

The solution of 20 grams of *p*-iodophenol in 200 c.c. of carbon tetrachloride was warmed to about 50°, and a stream of chlorine was passed into the solution. The iodo-dichloride, at first formed, rapidly decomposed with evolution of hydrogen chloride. The chlorination was continued until all evolution of hydrogen chloride had ceased; a dark-coloured solution was obtained. When the carbon tetrachloride had been distilled off, a dark product remained, which contained free iodine.

By steam distillation of this crude product the more volatile tetrachloro-*p*-iodophenol was easily obtained.

By fractional crystallisation of the crude product from light petroleum, white needles melting at 186—187° were obtained. Analysis showed this to be pentachlorophenol. (Found, Cl = 66·47. Calc., Cl = 66·60 per cent.)

Pentachlorophenol is described by Erdmann (*Annalen*, 1841, **37**, 343), Erdmann and Laurent (*Annalen*, 1843, **48**, 309), Schützenberger (*Bull. Soc. chim.*, 1865, [ii], **4**, 103), and by Weber and Wolf (*Ber.*, 1885, **18**, 335). The pentachlorophenol yielded an acetate melting at 147—148°, which is the melting point given by Weber and Wolf (*loc. cit.*).

Pentachlorophenyl Benzoate, $C_6Cl_5{\cdot}OBz$.

This compound was obtained in small, white needles melting at 159° after recrystallisation from absolute alcohol. It was almost insoluble in most solvents in the cold, and only sparingly soluble in hot alcohol:

0·1274 gave 0·2459 AgCl. Cl = 47·76.

$C_{13}H_5O_2Cl_5$ requires Cl = 47·91 per cent.

Hexachloro*cyclo*hexadienone resulted when *p*-iodophenol was chlorinated in warm solution, the solvent being carbon tetrachloride that had been employed for other chlorinations, and in the purification of which no special precautions had been taken. The solution was maintained at 50—60° during the chlorination. The solvent was distilled off, and the resulting product was recrystallised from methyl alcohol, when light, yellow tablets melting at 107° were obtained. The substance did not contain iodine, but on being added to potassium iodide solution immediately liberated iodine.

Analysis showed the compound to be hexachloro*cyclo*hexadienone, which has been described by Langer (*Annalen*, 1882, **215**, 122), Hugounenq (*Ann. Chim. Phys.*, 1890, [vi], **20**, 559), Morel (*ibid.*, 561), and Zincke and Schaum (*Ber.*, 1894, **27**, 546). (Found, Cl = 70·71. Calc., Cl = 70·76 per cent.)

By the action of potassium iodide on hexachloro*cyclo*hexadienone, pentachlorophenol was obtained, and iodine was liberated. This reaction was followed quantitatively, and it was found that 0·1561 gram gave 0·1314 gram of iodine. The equation $C_6Cl_6O + 2KI = C_6Cl_5OK + KCl + I_2$ requires 0·1317 gram of iodine.

Hexachloro*cyclo*hexadienone, by the action of sodium in methyl alcohol, gave the 1:3:3:4-tetramethyl ether of 1:3:3:4:4-trichloropentahydroxy*cyclo*hexadiene, melting at 142—143°, as described by Zincke and Schaum (*loc. cit.*).

Traces of chloroanil (melting at 282°) were also obtained in some cases. It was isolated on extracting with alcohol, in which it is only sparingly soluble.

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CI.—*Researches on the Constitution of Physostigmine. Part I.*

By Arthur Henry Salway.

The constitution of physostigmine (eserine), $C_{15}H_{21}O_2N_3$, is a subject of considerable interest on account of the valuable therapeutic properties which the alkaloid possesses. It has already been shown by Petit and Polonowsky (*Bull. Soc. chim.*, 1893, [iii], 9, 1008) that physostigmine is a monacidic tertiary base, and that it also contains a $CO\cdot NHMe$ complex, since carbon dioxide and methylamine are eliminated on heating with aqueous potassium hydroxide. Ehrenberg (*Verh. Ges. deut. Naturforsch. Aerzte*, 1893, ii, 102) independently confirmed the conclusions of Petit and Polonowsky, and also obtained from the alkaloid by the action of potassium hydroxide in the absence of air a new base, $C_{13}H_{18}ON_2$, to which the name of eseroline was given. Physostigmine was therefore stated by him to be a substituted carbamide, represented by the formula $(C_{13}H_{16}ON)NH\cdot CO\cdot NHMe$, and the action of alkalis on the alkaloid was represented by the equation:

$$(C_{13}H_{16}ON)NH\cdot CO\cdot NHMe + H_2O = C_{13}H_{16}ON\cdot NH_2 + CO_2 + NH_2Me.$$

Eseroline is therefore, according to Ehrenberg, an amino-derivative of the complex $C_{13}H_{16}ON$, but it should be pointed out that the action of alkalis on physostigmine would be equally well explained by assuming that the alkaloid is a urethane of the formula $NHMe\cdot CO\cdot O\cdot C_{13}H_{17}N_2$, in which case eseroline would be an alcohol, $C_{13}H_{17}N_2\cdot OH$.

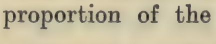
It is well known that physostigmine absorbs oxygen rapidly in the presence of alkalis, and is converted into oxidation products known as rubreserine, eserine brown, and eserine blue respectively. Ehrenberg (*loc. cit.*) has already shown that rubreserine possesses the formula $C_{13}H_{16}O_2N_2$, and that its formation from physostigmine depends on the primary conversion of the latter into eseroline according to the following scheme:

$$\underset{\text{Phyostigmine.}}{C_{15}H_{21}O_2N_3} \xrightarrow{\text{KOH}} \underset{\text{Eseroline.}}{C_{13}H_{18}ON_2} \xrightarrow{O_2} \underset{\text{Rubreserine.}}{C_{13}H_{16}O_2N_2}.$$

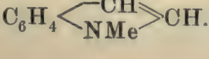
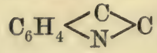
Little is otherwise known, however, regarding the chemical character of eseroline and rubreserine, whilst the so-called eserine blue and eserine brown have not previously been isolated in the pure condition. In view of these facts, it seemed evident that further information regarding the constitution of physostigmine would be obtained by a complete examination of eseroline and its oxidation products, and accordingly these substances have now been investigated.

Eseroline was found to be a strong base, which yields salts with only one equivalent of an acid. It contains one methyl group attached to nitrogen, and forms an additive product with one molecule only of methyl iodide, being therefore a tertiary base. Eseroline also possesses acidic properties, since it dissolves in aqueous sodium hydroxide without change in the absence of air. The state of combination of the oxygen atom in eseroline could not be determined with certainty, since the base did not react with semicarbazide or diazomethane, whilst attempts to prove the presence of a hydroxyl group by means of acetic anhydride led to indefinite products. Eseroline, in the presence of alkalis, was found to absorb 5 atoms of oxygen per molecule of the base. The first product of the oxidation, rubreserine, is formed by the rapid absorption of two atoms of oxygen. This compound, the formula of which has now been definitely established as $C_{13}H_{16}O_2N_2$, possesses both basic and acidic properties, and, unlike eseroline, readily reacts with diazomethane. If the oxidation is allowed to proceed further with free access of air or oxygen, the red colour of the rubreserine changes to yellowish-brown, with the formation of an indefinite mixture of degradation products. When the oxidation, on the other hand, proceeds slowly with a limited supply of air, the red solution gradually changes to an intense blue. This blue colour is due to the presence of a compound termed eserine blue, which has now been isolated in a pure state. It is a base which has the formula $C_{17}H_{23}O_2N_3$, and yields salts with two equivalents of an acid. Its formation appears to be due to the condensation of eseroline with a degradation product of this base.

In order to obtain further information regarding the structure of physostigmine, many attempts were made to resolve it into products having a less carbon content than that of eseroline and rubreserine. Hofmann's method of degradation by exhaustive methylation was applied to eseroline, but found impracticable on account of the ease with which eseroline methiodide is oxidised in the presence of alkalis, whilst the vigorous oxidation of physostigmine and eseroline under varied conditions yielded no definite compound. On the other hand, distillation of physostigmine with zinc dust gave a product which consisted of 2-methylindole,



$$C_6H_4{<}\begin{smallmatrix}CH\\NH\end{smallmatrix}{>}CMe,$$

together with a small proportion of the isomeric 1-methylindole,  $C_6H_4{<}\begin{smallmatrix}CH\\NMe\end{smallmatrix}{>}CH$. The formation of indole derivatives by the zinc dust distillation of physostigmine cannot be accepted, however, as definite proof of the presence of the  $C_6H_4<\substack{C\\N}>C$ complex, since indole is produced by the dry distillation of a number of nitrogen compounds in which the above complex is absent. Nevertheless, in all such instances, there is present a benzene nucleus attached to a nitrogen atom, and therefore physostigmine must also contain this atomic grouping.

It has now been shown that physostigmine contains the groups CO·NHMe, NMe, and NPh. Further investigations are contemplated, by which it is hoped that it may be possible to determine the character of the remaining part of the molecule, and also the relations existing between eseroline, rubreserine, and eserine blue.

EXPERIMENTAL.

The Preparation and Properties of Eseroline.

The preliminary experiments, undertaken with the object of ascertaining the best conditions for the preparation of eseroline, led to the ultimate adoption of the following method: Twenty grams of physostigmine dissolved in a little alcohol were introduced into a flask, and the air displaced from the latter by a current of hydrogen. An excess of sodium hydroxide (100 c.c. of a 10 per cent. solution) which had been freed from dissolved air by boiling was then added by means of a dropping funnel, and the mixture kept at the ordinary temperature for four hours with a constant stream of hydrogen passing through it. At the expiration of this time, ether was added, the mixture well shaken, and the ethereal layer then syphoned off, care being taken to avoid contact of air with the alkaline liquid in the flask. The process of extraction with ether was repeated many times (six to ten extractions were necessary) until no further basic matter was removed by this treatment. The ethereal extracts were then washed with a little water, dried, and carefully concentrated, the last portions of solvent being removed in a vacuum desiccator over potassium hydroxide. The oily residue which was thus obtained slowly crystallised after keeping for some time. The crystals were collected, washed with a little ether, and recrystallised from a mixture of benzene and petroleum, when the base separated in colourless prisms melting at 128°. The yield of pure substance amounted to 70 per cent. of the physostigmine employed. It was analysed with the following result:

0·1164 gave 0·3062 CO_2 and 0·0914 H_2O. C = 71·7; H = 8·7.
0·1426 „ 15·9 N_2 at 16° and 744 mm. N = 12·8.
$C_{13}H_{18}ON_2$ requires C = 71·6; H = 8·3; N = 12·8 per cent.

The empirical formula assigned to eseroline by Ehrenberg (*loc. cit.*) is thus confirmed.

The molecular weight of eseroline was next determined by the cryoscopic method in benzene:

0·2058 in 22·53 benzene gave $\Delta t - 0\cdot116^\circ$. M.W. = 394.
0·1792 „ 24·40 „ „ $\Delta t - 0\cdot093^\circ$. M.W. = 395.
$(C_{13}H_{18}ON_2)_2$ requires M.W. = 436.

It appears from these results that eseroline either possesses twice the molecular weight previously assigned to it, or is associated in benzene solution. A determination of the molecular weight of the base in nitrobenzene gave the following results:

0·1251 in 31·25 nitrobenzene gave $\Delta t - 0\cdot094^\circ$. M.W. = 298.
0·2459 „ 31·25 „ „ $\Delta t - 0\cdot164^\circ$. M.W. = 336.
$C_{13}H_{18}ON_2$ requires M.W. = 218.

It is to be inferred from these determinations that the simplest molecular formula of eseroline is $C_{13}H_{18}ON_2$, but that the base is associated in benzene solution and to a less extent also in nitrobenzene. Physostigmine, on the other hand, was found to give normal results, both in benzene and nitrobenzene.

A determination of the specific rotatory power of eseroline resulted as follows:

0·2736, made up to 20 c.c. with methyl alcohol, gave, in a 2-dcm. tube, $\alpha_D - 2^\circ 56'$, whence $[\alpha]_D - 107\cdot2^\circ$.

Eseroline is readily soluble in alcohol, ether, chloroform, or benzene, but only sparingly so in light petroleum. The free base is quite stable when pure, and can be kept for a long time exposed to the air without change. In neutral or acid solutions it is slowly oxidised, whilst in the presence of alkalis the oxidation is extremely rapid. On account of the ease with which it oxidises, eseroline possesses strong reducing properties, silver nitrate, gold chloride, and platinic chloride being reduced by it to the metallic state. Eseroline possesses a strongly alkaline reaction. Its basicity was ascertained by dissolving it in $N/10$-sulphuric acid, and titrating the excess of acid with barium hydroxide in the presence of ether, using iodeosin as indicator:

0·1791 required for neutralisation 8·15 c.c. $N/10$-H_2SO_4, whereas a monacidic base, $C_{13}H_{18}ON_2$, requires 8·2 c.c.

It is evident from this result that eseroline contains only one basic nitrogen atom.

Eseroline Hydrochloride.—This salt was prepared by passing dry hydrogen chloride into an ethereal solution of the base. The colourless precipitate which formed was collected and purified by crystallisation from a mixture of alcohol and ethyl acetate, when it was obtained in stellate clusters of colourless needles melting at 212°:

0·2772, heated at 110°, lost 0·0189 H_2O. $H_2O = 6·8$.

$C_{13}H_{19}ON_2Cl,H_2O$ requires $H_2O = 6·6$ per cent.

0·1071 gave 0·2406 CO_2 and 0·0756 H_2O. $C = 61·3$; $H = 7·8$.

0·0983* „ 0·0564 AgCl. $Cl = 14·2$.

$C_{13}H_{19}ON_2Cl$ requires $C = 61·3$; $H = 7·5$; $Cl = 14·0$ per cent.

Eseroline picrate crystallises from alcohol in stellate clusters of yellow needles melting at 195°:

Eseroline possesses feeble acidic properties, since it is readily soluble in alkali hydroxides, and can be recovered from the alkaline solution unchanged in the absence of air. It contains one methylimide group, NMe, the presence of which was proved by the method of Herzig and Meyer (*Monatsh.*, 1895, **18**, 379):

0·1208 gave 0·0986 AgI. $NMe = 11·4$.

$C_{12}H_{15}ON(NMe)$ requires $NMe = 13·3$ per cent.

In order to obtain if possible some knowledge of the state of combination of the oxygen atom of eseroline, the latter was treated with semicarbazide hydrochloride in dilute alcohol and the mixture kept for some time, but no reaction took place. Diazomethane in ethereal solution was likewise without action on eseroline. Acetic anhydride, on the other hand, appears to produce some change, but no definite product could be isolated from the reaction mixture. It would appear from these results that eseroline does not contain a carbonyl group, whilst the presence of a hydroxyl group is doubtful.

Eseroline Methiodide.—When methyl iodide is added to a solution of eseroline in chloroform, reaction takes place with evolution of heat, and a crystalline precipitate immediately separates. This substance crystallises from water in thin, colourless needles melting at 196°:

0·1208 gave 0·2079 CO_2 and 0·0652 H_2O. $C = 46·9$; $H = 6·0$.

$C_{14}H_{21}ON_2I$ requires $C = 46·7$; $H = 5·8$ per cent.

It is evident that the above compound is formed by the combination of one molecule of methyl iodide with one molecule of eseroline. The same compound is produced when an excess of methyl iodide is employed in the reaction; eseroline must therefore be a tertiary base.

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* The amount of chlorine in eseroline hydrochloride cannot be determined by simple precipitation with aqueous silver nitrate, since the latter is reduced by eseroline in the absence of nitric acid, whilst, in the presence of this acid, eseroline is decomposed with the formation of hydrocyanic acid, which forms, with the silver nitrate, a precipitate of silver cyanide. The result recorded above was obtained by the Carius method.

Eseroline methiodide is readily soluble in alcohol, but only sparingly so in chloroform and acetone. The quaternary ammonium base produced from it by the addition of alkalis is very unstable, being readily oxidised in the presence of air with the formation of a deep red solution. On account of this property it was found impractical to obtain information regarding its structure by means of Hofmann's method for the degradation of quaternary ammonium bases.

The Oxidation Products of Physostigmine and Eseroline.

As a preliminary experiment the amounts of oxygen absorbed by both physostigmine and eseroline were quantitatively determined by the following method: A quantity of oxygen was collected in a graduated burette over an aqueous solution of sodium hydroxide, and the volume, temperature, and pressure of the gas observed. The base to be examined (about 0·05 gram) was then introduced in a small glass capsule, the burette tightly corked, and the contents were agitated vigorously. By opening the burette from time to time under an aqueous solution of sodium hydroxide, the decrease in volume of the oxygen could be determined. The agitation of the mixture was continued until no further appreciable decrease in volume at constant temperature and pressure took place. The results of a number of concordant determinations obtained by this method are embodied in the following table:

	Atoms of oxygen absorbed per molecule.	
Time.	Physostigmine.	Eseroline.
10 minutes	—	1·37
1 hour	1·19	3·80
2 hours	2·46	4·41
3 ,,	3·49	4·68
5 ,,	4·51	4·80
7 ,,	4·70	4·98
20 ,,	5·03	5·02

When physostigmine and eseroline were oxidised in the manner described above, the alkaline solution immediately became red at the commencement of the oxidation, and the intensity of this colour continued to increase until approximately 2 atoms of oxygen had been absorbed. The colour then gradually changed from red to brown, and after 5 atoms of oxygen had been absorbed, became brownish-yellow. No trace of eserine blue was formed by this method of oxidation.

Preparation and Properties of Rubreserine.

It would appear from the above results that the preparation of rubreserine would be best effected by arresting the oxidation of eseroline after two atoms of oxygen had been absorbed. In order to achieve this object, 30 c.c. of a 1 per cent. solution of potassium hydroxide were introduced in a flask full of oxygen, and the latter connected with a small oxygen gasometer, by means of which any absorption of gas could be measured. A weighed quantity of eseroline (1 gram at each oxidation) was then quickly added, and the contents of the flask vigorously shaken. After the requisite volume of oxygen had been absorbed as indicated by the gasometer, sulphuric acid was added in an amount just sufficient to neutralise the potassium hydroxide, and the mixture then thoroughly extracted with chloroform. The chloroform solution was washed with a little water, dried, and the solvent removed, when a deep red residue, which rapidly solidified, was obtained. The substance was purified by crystallisation, first from a mixture of petroleum and chloroform, and finally from water:

0·0932 lost 0·0067 H_2O. $H_2O = 7·2$.

$C_{13}H_{16}O_2N_2,H_2O$ requires $H_2O = 7·2$ per cent.

0·0865 gave 0·2142 CO_2 and 0·0560 H_2O. $C = 67·5$; $H = 7·2$.

0·0631 „ 6·8 c.c. N_2 at 24° and 750 mm. $N = 12·1$.

$C_{13}H_{16}O_2N_2$ requires $C = 67·2$; $H = 6·9$; $N = 12·1$ per cent.

The molecular weight of rubreserine was determined* by Barger's microscopic method, which gave the following result:

0·0648 in 0·8422 alcohol was between 0·275 mol. and 0·300 mol.

Mean M.W. = 268. $C_{13}H_{16}O_2N_2$ requires M.W. = 232.

These results confirm the formula originally assigned to rubreserine by Ehrenberg.

Rubreserine crystallises from water in deep red needles, containing 1 molecule of water of crystallisation. It is stated by Eber (*Pharm. Zeit.*, 1888, **33**, 611) to melt at 138°, but the present author has not been able to confirm this melting point. The air-dried substance was found to melt indefinitely at 113—125°, but when the water of crystallisation was removed in a vacuum desiccator over potassium hydroxide the substance then melted at 152°. Rubreserine is insoluble in light petroleum or ether, but readily soluble in water, alcohol, or chloroform, giving blood-red solutions. It is moderately soluble in hot benzene, and crystallises from this solvent in red needles, which melt at 100° and contain benzene of crystallisation. It dissolves in concentrated sulphuric acid with a yellow colour, which becomes red on the addition of water. The aqueous solution of rubreserine is readily decolorised by reducing agents such as hydrogen sulphide, but the red colour reappears on removing the latter by a current of air. When anhydrous rubreserine is heated for a few hours at 115°, the colour changes from red to brown, and finally becomes quite black without alteration in weight. The product does not melt below 300°, and is undoubtedly a polymerised form of rubreserine. Rubreserine is neutral in reaction towards litmus, but it possesses both basic and acidic properties. Its basic properties were proved by the formation of a hydrochloride, picrate, and aurichloride respectively.

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* The author wishes to express his thanks to Mr. A. J. Ewins, who has kindly conducted this determination.

Rubreserine Hydrochloride.—This substance was prepared by passing dry hydrogen chloride into a solution of rubreserine in ethyl acetate containing a little alcohol. A dull red, crystalline precipitate was thus obtained, which melted and decomposed at 185°:

0·0992, heated at 110°, lost 0·0070 H_2O. $H_2O = 7·1$.

$C_{13}H_{17}O_2N_2Cl,H_2O$ requires $H_2O = 6·3$ per cent.

0·0912 * gave 0·1942 CO_2 and 0·0558 H_2O. $C = 58·1$; $H = 6·8$.

$C_{13}H_{17}O_2N_2Cl$ requires $C = 58·1$; $H = 6·3$ per cent.

Rubreserine picrate crystallises from dilute alcohol in brick-red leaflets, which begin to change at 186°, and completely decompose at 198°.

Rubreserine Aurichloride.—This substance separates from a solution of rubreserine in hydrochloric acid, to which gold chloride had been added, in bright red needles, which decompose at 190—195°:

0·1710 gave 0·1705 CO_2, 0·0442 H_2O, and 0·0595 Au. $C = 27·2$; $H = 2·9$; $Au = 34·8$.

$C_{13}H_{17}O_2N_2,AuCl_4$ requires $C = 27·3$; $H = 3·0$; $Au = 34·4$ per cent.

It is evident from the examination of the above salts that rubreserine, like physostigmine and eseroline, contains only one basic nitrogen atom.

The acidic properties of rubreserine were indicated by the formation of a silver salt; thus, when silver nitrate was added to an aqueous solution of rubreserine, the silver salt of rubreserine nitrate separated in dull red needles, which possess a bronze-like lustre:

0·0819 gave 0·1170 CO_2, 0·0316 H_2O, and 0·0221 Ag. $C = 39·0$; $H = 4·3$; $Ag = 27·0$.

$C_{13}H_{16}O_2N_2,AgNO_3$ requires $C = 38·8$; $H = 4·0$; $Ag = 26·9$ per cent.

Further evidence of the acidic character of rubreserine was afforded by its behaviour towards diazomethane. An ethereal solution of this reagent rapidly changed rubreserine dissolved in a little alcohol from red to yellow with evolution of nitrogen. From the reaction mixture, however, only a very small quantity of a homogeneous substance could be isolated. This was a base obtained in the form of a hydrochloride, which crystallised in stellar clusters of colourless needles decomposing at 185°. It is evident from the method of preparation of this compound that it is the hydrochloride of a methyl derivative of rubreserine, but the yield was too small for further examination.

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* Anhydrous substance.

Rubreserine is unstable in the presence of alkali hydroxides; when agitated with sodium hydroxide in the presence of air or oxygen the red colour of the rubreserine is changed first to brown and then to brownish-yellow. In this reaction a mixture of products is formed, from which no definite substance could be separated. It is evident, therefore, that the so-called eserine brown is not a homogeneous compound.

Isolation of Eserine Blue, $C_{17}H_{23}O_2N_3$.

In the course of the preliminary experiments on the oxidation of physostigmine it was observed that the blue coloration was only produced when oxidation proceeded slowly with a limited supply of air or oxygen. In view of this fact, the method adopted for the preparation of the blue compound was as follows: A quantity of physostigmine (1 gram) dissolved in a little alcohol was added to an aqueous solution of barium hydroxide in a small flask, so that the latter contained about three parts of liquid to one part of air. The flask was then closed, and kept for some time. The oxygen in the flask was soon absorbed, and the solution became red with the formation of rubreserine, but after keeping a few hours the red colour changed to green and then to blue, when more air was admitted and the vessel again closed. The mixture was thus supplied at intervals with oxygen, care being taken, however, that the solution never became red by too rapid oxidation. This process was continued for several days until a test portion, when freely exposed to the air, did not change its blue colour. The blue solutions obtained from several such oxidations were united and thoroughly extracted with chloroform. The chloroform extract, which was intensely blue, was washed with a little water, and then agitated with successive small portions of $N/10$-hydrochloric acid until the solution became acid to litmus.* The first few extracts were deep blue by transmitted light, but purple-red by reflected light; from these no pure substance could be isolated, and they evidently contained a mixture of bases. The final extracts, however, were deep blue, both by transmitted and reflected light. They were united, then evaporated to dryness under diminished pressure, and the residue dissolved in a little hot alcohol, when, on cooling, a crystalline hydrochloride separated in deep blue needles. The yield of this compound was equivalent to about 8 per cent. of the physostigmine employed in the reaction:

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* The chloroform solution remaining after this treatment contained a small quantity of rubreserine.

0·0708 gave 0·1419 CO_2 and 0·0465 H_2O. C = 54·7; H = 7·3.
0·0913 „ 8·7 N_2 at 18° and 764 mm. N = 11·2.
0·0888 „ 0·0686 AgCl. Cl = 19·1.

Another preparation of the blue hydrochloride gave the following numbers:

0·1120 gave 0·2247 CO_2 and 0·0694 H_2O. C = 54·7; H = 6·9.
$C_{17}H_{25}O_2N_3Cl_2$ requires C = 54·5; H = 6·7; N = 11·2;
Cl = 19·1 per cent.

The free base corresponding with this hydrochloride was prepared by treating the latter with dilute sodium hydroxide, and extracting the alkaline liquid with chloroform. On the addition of light petroleum to the dry chloroform solution the base separated as a dark blue powder, which was not obtained in the crystalline condition:

0·0310 gave 0·0766 CO_2 and 0·0222 H_2O. C = 67·4; H = 8·0.
$C_{17}H_{23}O_2N_3$ requires C = 67·8; H = 7·6 per cent.

An attempt was made to determine the molecular weight of the above base by the microscopic method, but owing to the intensity of the blue colour a satisfactory determination was not possible. It is evident, however, from the above analyses, that the simplest formula for the compound is $C_{17}H_{23}O_2N_3$.

Eserine blue is a dark blue powder, which is readily soluble in water, chloroform, or alcohol with the formation of intensely blue solutions. When the aqueous solution is heated with alkali hydroxides, an insoluble black powder separates. Eserine blue is a strong base, which forms salts with two equivalents of an acid.

The *hydrochloride*, $C_{17}H_{23}O_2N_3,2HCl$, prepared as described above, crystallises in blue needles, which by reflected light have a bronze-like lustre. It is readily soluble in water, yielding a deep blue solution, but on the addition of a little acid a beautiful carmine-red fluorescence is produced.

The *aurichloride* was prepared by the addition of gold chloride to a solution of the base in hydrochloric acid. The violet precipitate thus obtained crystallised from hot alcohol containing a little hydrochloric acid in minute, violet prisms, which began to decompose at 165°:

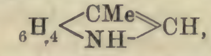
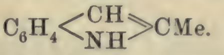
0·1671 gave 0·0666 Au. Au=39·9.

$C_{17}H_{25}O_2N_3(AuCl_4)_2$ requires Au=40·2 per cent.

Eserine blue can also be prepared by the slow oxidation of eseroline in the presence of alkalis, but it does not appear to be formed when pure rubreserine is oxidised. In view of these facts it seems probable that the formation of eserine blue is due to the condensation of eseroline with a degradation product of this base. An attempt was therefore made to obtain from physostigmine products having a carbon content lower than that of eseroline and rubreserine, but although experiments were conducted with various oxidising agents under diverse conditions, no definite compound was obtained.

Formation of Indole Derivatives from Physostigmine.

Fifteen grams of physostigmine were intimately mixed with ten times its weight of zinc dust, and the mixture strongly heated, in convenient portions, in a combustion tube in a current of hydrogen. The products of the distillation were first conducted over red-hot pumice, which had been impregnated with zinc dust, and then condensed in a receiver immersed in a freezing mixture, when a quantity of an ammoniacal liquid, together with a brown, viscid, oily substance, collected in the receiver. The oily substance was separated from the ammoniacal liquid, and then distilled in a current of steam. A pale yellow, volatile oil passed over in the steam distillate, whilst a small amount of a non-volatile, brown, resinous substance remained in the flask. The volatile oil was dissolved in ether, the ethereal solution washed with a little dilute hydrochloric acid, then dried, and the solvent removed. The yellow oil thus obtained amounted to 5—10 per cent. of the physostigmine employed in the distillation. It possessed the characteristic odour of indole compounds, and yielded a cherry-red coloration with a pine shaving which had been moistened with hydrochloric acid. It was insoluble in dilute acids, but dissolved in concentrated hydrochloric acid with the formation of a yellow solution, from which a resinous substance separated on heating. It gave a red coloration with sodium nitrite and glacial acetic acid, whilst with a trace of bromine water an evanescent, blue coloration was produced. The boiling point of the compound was determined by Schleiermacher's method (*Ber.*, 1891, **24**, 944) applicable to small quantities of substance, and found to be 268°. The substance after redistillation was analysed. (Found, C=82·0; H=7·3; N=10·5. C_9H_9N requires C=82·4; H=6·9; N=10·7 per cent.)

The above analyses and the properties of the substance indicate that it is a methyl derivative of indole. It is not identical with 3-methylindole,  $C_6H_4<\substack{CMe\\NH}>CH$, since the latter dissolves in concentrated hydrochloric acid with a violet colour. The properties of the substance, as described above, are identical with those of 2-methylindole,  $C_6H_4<\substack{CH\\NH}>CMe$. The latter compound, however, melts at 59°, whilst the above product did not solidify in the cold. This behaviour was found to be due to the presence of the isomeric 1-methylindole, since on heating the substance with hydriodic acid at 200—300° methyl iodide was liberated. The amount of 1-methylindole was ascertained by a quantitative determination of the methylimido-group, when the result indicated the presence of 15 per cent. of this compound. It is evident, therefore, that physostigmine, when distilled with zinc dust, yields 2-methylindole with a small quantity of 1-methylindole.

The ammoniacal bases formed in the distillation were carefully examined, and found to consist almost entirely of ammonia. Petit and Polonowsky (*loc. cit.*) state to have obtained a phenolic substance, melting at 108°, by the distillation of physostigmine with zinc dust, but no trace of this compound could be isolated in the above experiment.

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CII.—1:3-*Keto-enolic Ethers and Derivatives of Dibenzoylmethane.*

By ROBERT DUNCOMBE ABELL.

THE object of this work, begun early in 1900, was to prepare ethers of the keto-enolic forms of the 1:3-diketones of the type

$$\cdot C(OR)\colon CH\cdot CO\cdot$$

by the silver oxide and alkyl iodide method, which did not appear to have been applied to the 1:3-keto-enols, phenyl α-hydroxystyryl ketone, OH·CPh:CH·COPh, one of the most stable of these 1:3-keto-enols, being chosen for the investigation.

Ethers of the keto-enolic forms of the 1:3-diketones were not known with certainty. Pond, Maxwell, and Norman (*Amer. Chem.*

J., 1899, **21**, 955) had described an unstable oil, which had been obtained by the action of sodium methoxide on one of the phenyl styryl ketone dibromides, CHPhBr·CHBr·COPh, as being probably the unsaturated ether, OMe·CPh:CH·COPh. This was confirmed by Pond, Yorke, and Moore (*Amer. Chem. J.*, 1901, **23**, 789), and a probable phenyl *α*-ethoxy-*p*-methoxystyryl ketone,

$$MeO·C_6H_4·C(OEt):CH·COPh,$$

was described by Pond and Shoffstall (*Amer. Chem. J.*, 1900, **22**, 658).

The action of silver oxide and methyl iodide on phenyl *α*-hydroxystyryl ketone gave *αα*-dibenzoylethane, $(C_6H_5·CO)_2·CH·CH_3$, which had also been obtained (i) by the action of methyl iodide on the sodium derivative of phenyl *α*-hydroxystyryl ketone (Beyme, *Diss.*, Leipzig, 1900) (compare p. 995); (ii) by the condensation of phenyl ethyl ketone with ethyl benzoate by means of sodium (Abell, *Diss.*, Leipzig, 1902). Miss Smedley (Trans., 1910, **97**, 1492) failed to condense these two substances by means of sodamide in ethereal solution.

Phenyl *α*-hydroxystyryl ketone reacted with silver oxide and ethyl iodide to give: (i) *αα*-dibenzoylpropane,

$$CHBz_2·CH_2·CH_3,$$

and (ii) a 17 per cent. yield of a substance isomeric with it, which crystallised in prisms melting at 77·5—78°, and was identified as phenyl *α*-ethoxystyryl ketone, OEt·CPh:CH·COPh, identical with the substance described by Ruhemann and Watson (Trans., 1904, **85**, 456) and by Sluiter (*Rec. trav. chim.*, 1905, [ii], **24**, 368).

From the above results it was concluded that the silver oxide and alkyl iodide method was not suitable for the formation of the ethers of phenyl *α*-hydroxystyryl ketone.

Of other methods tried, it was found that the methyl and ethyl ethers could be obtained in good yield by the action of sodium methoxide and ethoxide respectively on phenyl *α*-bromostyryl ketone, CPhBr:CH·COPh, under suitable conditions. Excess of alkyl oxide and prolonged heating must be avoided if the product is to be free from phenyl *α*-hydroxystyryl ketone. Phenyl styryl ketone was always a product of these reactions. Sluiter (*loc. cit.*) used this method, but did not record the formation of phenyl styryl ketone, and stated that the ethyl ether could be obtained from phenyl *α*-bromostyryl ketone by means of sodium only in 96 per cent. or more concentrated alcohol.

This, however, is incorrect, since sodium hydroxide in 90 per cent., and even in 70 per cent., alcohol gave the *α*-ethoxy-compound, but in diminished quantity, and the amount of phenyl styryl ketone was proportionately greater (see p. 1003).

Again, Sluiter (*loc. cit.*) found that after distilling the crude ethyl ether under diminished pressure, the distillate melted at 61° instead of 77°. This he regarded as an isomeric phenyl α-ethoxystyryl ketone, which was unstable, and gradually changed to the stable isomeride, melting at 77°. He found for the labile form C=80·3 and 80·7, instead of C=80·95 per cent.

Having prepared the ethyl ether several times by this means, the author has failed to confirm the existence of Sluiter's labile form, and attributes the low melting point to the presence of phenyl styryl ketone, from which the ethyl ether cannot be separated by distillation.

The methyl ether of phenyl α-hydroxystyryl ketone can be obtained pure only with difficulty, and is stable only when pure. The methyl ether forms the same derivatives as phenyl α-hydroxystyryl ketone and as the ethyl ether ("dibenzoylmethane," *Annalen*, 1899, **308**, 219).

The sodium derivative of phenyl α-hydroxystyryl ketone reacted, under suitable conditions, with:

(1) Methyl iodide to give αα-dibenzoylethane. Beyme (*loc. cit.*) using the same method gave insufficient detail for success.

(2) Ethyl iodide to form αα-dibenzoylpropane.*

(3) Ethyl iodoacetate to produce *ethyl β-dibenzoylpropionate*, $CHBz_2\cdot CH_2\cdot CO_2Et$.

(4) Iodine to form s-*tetrabenzoylethane*, $CHBz_2\cdot CHBz_2$, and *dibenzoyliodomethane*, $CHIBz_2$, both of which give a reddish-brown coloration with ferric chloride, and a green, crystalline precipitate with an alcoholic solution of copper acetate.

(5) Benzyl chloride to give benzoic acid and benzylacetophenone, $C_6H_5\cdot CO\cdot CH_2\cdot CH_2\cdot C_6H_5$, the decomposition products of the expected αα-dibenzoyl-β-phenylethane, $CHBz_2\cdot CH_2Ph$, which has been obtained by the use of benzyl iodide.

(6) Benzoyl chloride to form the α- or diketo-enolic form of tribenzoylmethane, $(C_6H_5\cdot CO)_2\cdot C\colon C(OH)\cdot C_6H_5$, and not the β- or triketo-form as stated by Claisen (*Annalen*, 1896, **291**, 95).

In these reactions, experimental details must be strictly followed; otherwise the yield of substance will be greatly diminished, and may even be nil; thus in the reaction with:

(1) Methyl iodide, phenyl ethyl ketone and methyl benzoate may be formed as the only products.

(2) Ethyl iodide, the products may be phenyl propyl ketone and ethyl benzoate. It is probably for this reason that Miss Smedley, having failed to obtain dibenzoylpropane, stated (Trans., 1910, **97**, 1492) that "αα-dibenzoylpropane cannot be directly prepared from

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* This was completed in 1903, two years before Sluiter's work appeared.

dibenzoylmethane by ethylation"; but gave no account of experimental conditions or of the products which were obtained.

(3) Ethyl iodoacetate, the substances formed may be benzoic acid and ethyl β-benzoylpropionate, $CH_2Bz \cdot CH_2 \cdot CO_2Et$.

EXPERIMENTAL.

Action of Methyl Iodide and Silver Oxide on Phenyl α-Hydroxystyryl Ketone.

Five grams of dry silver oxide (2 mols.) were added to a solution of 5 grams of phenyl α-hydroxystyryl ketone in 19 grams of methyl iodide (6 mols.). After the spontaneous reaction had ceased, the mixture was heated on the water-bath for an hour. Dry ether was added, the solution filtered, and evaporated in a current of dry air. The pink-coloured crystalline residue, when recrystallised from alcohol, gave a small quantity of unchanged phenyl α-hydroxystyryl ketone and an almost quantitative yield of *αα*-dibenzoylethane, $C_{16}H_{14}O_2$, which crystallised in colourless needles melting at 83—84°. (Found, C=80·59; H=5·93. Calc., C=80·67; H=5·88 per cent.)

Action of Ethyl Iodide and Silver Oxide on Phenyl α-Hydroxystyryl Ketone.

A mixture of 5 grams of phenyl α-hydroxystyryl ketone, 20 grams of ethyl iodide, and 5 grams of dry silver oxide became hot spontaneously. The mixture when treated as above gave a crystalline residue, which was separated by alcohol into (i) colourless needles of *αα*-dibenzoylpropane, $C_{17}H_{16}O_2$, which melted at 87° (Found, C=80·90; H=6·45. Calc., C=80·95; H=6·35 per cent.); (ii) a red oil, from which a small quantity of phenyl α-hydroxystyryl ketone was separated by the addition of an alcoholic solution of copper acetate. The alcoholic filtrate was distilled, and the residue dissolved in ether and water. The washed and dried ethereal solution gave an oil which was distilled under diminished pressure to remove a few drops of a colourless, mobile oil boiling at 110—112°/20 mm., which was identified as phenyl propyl ketone, $C_{10}H_{12}O$, by means of its semicarbazone, m. p. 186—187°. (Found, N=20·64. Calc., N=20·49 per cent.)

The residue in the flask when crystallised from light petroleum (b. p. 70—80°) gave 1 gram of a substance which formed colourless prisms melting at 77·5—78°. This substance was identified as phenyl α-ethoxystyryl ketone, $OEt \cdot CPh \colon CH \cdot COPh$ (compare Ruhemann and Watson, *loc. cit.*, and Sluiter, *loc. cit.*), by its properties, decomposition products, and analysis. (Found, C=80·85; H=6·48. Calc., C=80·95; H=6·35 per cent.)

The above methods having failed to give the desired ethers, it appeared possible to obtain the ethyl and methyl ethers from phenyl α-bromostyryl ketone, CBrPh:CH·COPh, by the action of sodium ethoxide or methoxide respectively, or from the sodium derivative of phenyl α-hydroxystyryl ketone with ethyl or methyl iodide.

Action of Sodium Ethoxide on Phenyl α-Bromostyryl Ketone.

Absolute alcoholic solutions of phenyl α-bromostyryl ketone (1 mol.) and sodium ethoxide (1 mol.) were mixed and allowed to remain at the ordinary temperature (four days), or were heated on the water-bath (a few minutes) until the solution ceased to show an alkaline reaction towards litmus. Water and ether were added, and the washed and dried ethereal solution, on evaporation, left an oil which was free from phenyl α-hydroxystyryl ketone. This oil crystallised when kept over sulphuric acid in an exhausted desiccator, or when distilled at 227—230°/20 mm. became crystalline in a few hours. On recrystallisation from alcohol the product gave (i) a good yield of phenyl α-ethoxystyryl ketone, crystallising in prisms (m. p. 77·5—78°) (Found, C=80·79; H=6·48. Calc., C=80·95; H=6·35 per cent.); (ii) a small amount of an oil which was completely converted into a crystalline product when brominated in carbon disulphide solution. Recrystallisation of this product from alcohol gave a small quantity of phenyl styryl ketone dibromide, CHPhBr·CHBr·COPh (m. p. 158°), and a large quantity of dibenzoylbromomethane, $CHBrBz_2$ (m. p. 92°), or dibenzoyldibromomethane, CBr_2Bz_2 melting at 94°. This oil was therefore a mixture of phenyl styryl ketone and phenyl α-ethoxystyryl ketone.

Action of Sodium Methoxide on Phenyl α-Bromostyryl Ketone.

The preparation of the methyl ether offered greater difficulties. In the first attempt a solution of 5 grams of phenyl α-bromostyryl ketone and 0·4 gram of sodium in methyl alcohol ceased to have an alkaline reaction after being warmed on the water-bath for two minutes. Phenyl α-hydroxystyryl ketone (m. p. 77—77·5°), in almost quantitative yield, and a small quantity of a yellow oil, which was not examined, were obtained.

Five further preparations, in which greater care was taken with the quantities of the reacting substances, for example, in one case, 12·5 grams of phenyl α-bromostyryl ketone with 73 c.c. of a solution of sodium methoxide in methyl alcohol (0·985 gram of sodium;

theory = 1 gram), gave a reddish-yellow oil boiling at 218°/15 mm. [Sluiter (*loc. cit.*) gives 220—222°/16 mm.], which contained a trace of bromine, but was quite free from phenyl α-hydroxystyryl ketone. After a few days, however, the specimens gave a decided red coloration with ferric chloride, a green, crystalline precipitate with an alcoholic solution of copper acetate, and in four to six weeks crystals of phenyl α-hydroxystyryl ketone separated. This was precipitated as its copper derivative, and the remaining oil, when brominated in carbon disulphide solution, gave minute quantities of phenyl styryl ketone dibromide (m. p. 158°) and phenyl α-bromostyryl ketone dibromide (m. p. 101°) (Crowther, *Diss.*, Leipzig, 1901), and a quantity of dibenzoylbromomethane or of dibenzoyldibromomethane. This oil therefore contains phenyl styryl ketone, its α-bromo- and α-methoxy-derivatives respectively.

What appeared to be the purest of the above preparations was analysed (Found, OMe = 12·2. OMe·CPh:CH·COPh requires OMe = 13·02 per cent.). Crystals of phenyl α-hydroxystyryl ketone separated from it after about three months.

A specimen of the methyl ether prepared in September, 1909, which showed no indication of change two years later, was obtained from 28·7 grams of pure phenyl α-bromostyryl ketone dissolved in methyl alcohol and 91 c.c. of an absolute methyl-alcoholic solution of sodium methoxide (2·302 grams of sodium). The mixture was heated on the water-bath for an hour, then precipitated with water, and extracted with ether. The reddish-yellow oil, which was obtained from the washed and dried ethereal solution, distilled at 218°/17 mm. (Found, OMe = 13·34. Calc., OMe = 13·02 per cent.)

This, the most permanent specimen of the methyl ether obtained by the author, has been used in the examination of its derivatives. With free hydroxylamine it gave an *oxime*, $CPh(:NOH)\cdot CH_2\cdot COPh$ (m. p. 165°), and 3:5-diphenyl*iso*oxazole (m. p. 140°). Hydroxylamine hydrochloride causes the formation of the latter compound only. Phenylhydrazine gave 1:3:5-triphenylpyrazole (m. p. 137°), bromine (1 mol.) gave dibenzoylbromomethane (m. p. 92°), whilst 2 molecular proportions of bromine gave dibenzoyldibromomethane (m. p. 94°).

These derivatives correspond with those obtained from phenyl α-hydroxystyryl ketone and "dibenzoylmethane" described by Wislicenus (*loc. cit.*). Bromine, however, reacts less readily with the methyl ether than with the other substances, but with the remaining reagents there is no marked difference in the rate of reaction.

aa-Dibenzoylethane, $CHBz_2 \cdot CH_3$.

aa-Dibenzoylethane has been prepared by the condensation of phenyl ethyl ketone with ethyl benzoate (Abell, *Diss.*, Leipzig, 1902); by the oxidation of 1:3-dihydroxy-1:3-diphenyl-2-methylpropane, $OH \cdot CHPh \cdot CHMe \cdot CHPh \cdot OH$ (Abell, Trans., 1901, **79**, 921; *Diss.*, Leipzig, 1902); from phenyl *a*-hydroxystyryl ketone by the action of methyl iodide and silver oxide (p. 992); and by the action of methyl iodide on the sodium derivative of phenyl *a*-hydroxystyryl ketone (Beyme, *loc. cit.*). Beyme gave insufficient practical detail to obtain a good yield. The author has found that the following procedure gave the best results.

Ten grams of phenyl *a*-hydroxystyryl ketone were added to a solution of 1 gram of sodium in 50 c.c. of absolute alcohol. The sodium derivative which separated as a yellowish-white solid was broken up by means of a glass rod, 10 grams of methyl iodide (1½ mols.) were added, and the mixture was heated on the water-bath under reflux until the solution was no longer alkaline to litmus. It was then poured into water, and extracted with ether, when the oil, obtained by evaporating the washed and dried ethereal solution, crystallised almost completely. The oily portion, which was removed by means of porous plate, consisted of phenyl ethyl ketone and methyl benzoate. The needle-shaped crystals formed an almost quantitative yield of dibenzoylethane (m. p. 83°). The aqueous solution contained traces of benzoic acid and of phenyl *a*-hydroxystyryl ketone.

In this preparation, excess of alkali and prolonged heating must be avoided; either will cause decomposition of the dibenzoylethane, and even with all possible care a portion of it is lost.

Dibenzoylethane was decomposed quantitatively by a hot alcoholic solution of potassium hydroxide (1 mol.) to benzoic acid and phenyl ethyl ketone.

aa-Dibenzoylpropane, $CHBz_2 \cdot CH_2 \cdot CH_3$.

Ten grams of phenyl *a*-hydroxystyryl ketone, 1 gram of sodium, 50 c.c. of absolute alcohol, and 10 grams of ethyl iodide under similar conditions gave an almost quantitative yield of dibenzoylpropane (m. p. 87°). A small quantity of the *a*-hydroxy-compound was recovered, and small amounts of phenyl propyl ketone, ethyl benzoate, and benzoic acid were recognised as products.

Again great care must be exercised in carrying out the reaction, as the following will show: Twelve grams of phenyl *a*-hydroxystyryl ketone were added to a solution of 1·5 grams of sodium (theory = 1·2 grams) in 50 c.c. of absolute alcohol. After the further addition of 20 grams of ethyl iodide (theory = 8·4 grams), the mixture was heated on the water-bath for two hours, and worked up as above. The product was distilled under diminished pressure, and gave:

(i) A colourless, mobile oil, b. p. 95—110°/13 mm., which was a mixture of almost equal quantities of phenyl propyl ketone and ethyl benzoate.

(ii) A minute quantity of a reddish-coloured residue, which was identified as phenyl α-hydroxystyryl ketone.

This probably accounts for Miss Smedley's statement (*loc. cit.*) that "$\alpha\alpha$-dibenzoylpropane cannot be directly prepared from dibenzoylmethane * by ethylation."

Dibenzoylpropane was decomposed quantitatively into phenyl propyl ketone and benzoic acid by an alcoholic solution of potassium hydroxide.

Ethyl β-Dibenzoylpropionate, $CHBz_2{\cdot}CH_2{\cdot}CO_2Et$.

Ten grams of phenyl α-hydroxystyryl ketone were added to a solution of 1 gram of sodium in 50 c.c. of absolute ethyl alcohol. After breaking up the sodium derivative which separated, 12 grams of ethyl iodoacetate (theory = 10 grams) were added, and the mixture was heated until no longer alkaline to litmus (fifteen minutes). Water and ether were then added, and the washed and dried ethereal solution gave:

(i) Ethyl iodoacetate. (ii) Ethyl β-benzoylpropionate (b. p. 163—165°/10 mm. Found, C = 69·84; H = 6·91. Calc., C = 69·91; H = 6·79 per cent.).

(iii) A residue of *ethyl β-dibenzoylpropionate*,

$$CHBz_2{\cdot}CH_2{\cdot}CO_2Et,$$

which crystallised from light petroleum in dense prisms melting at 82—83°:

0·201 gave 0·542 CO_2 and 0·1088 H_2O. C = 73·53; H = 6·01.

$C_{19}H_{18}O_4$ requires C = 73·55; H = 5·81 per cent.

The aqueous solution contained traces of benzoic acid and phenyl α-hydroxystyryl ketone.

Ethyl β-dibenzoylpropionate is rapidly decomposed in the above preparation by heat. One preparation, which was heated for twenty minutes, gave a small yield of ethyl β-dibenzoylpropionate and relatively large quantities of its decomposition products: ethyl β-benzoylpropionate and benzoic acid.

Ethyl β-dibenzoylpropionate was decomposed by potassium hydroxide in aqueous, or more rapidly in alcoholic, solution according to the equation:

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* The dibenzoylmethane here referred to is phenyl α-hydroxystyryl ketone.

$$CHBz_2{\cdot}CH_2{\cdot}CO_2Et + 2KOH = \\ C_2H_5{\cdot}OH + H_2O + C_6H_5{\cdot}CO_2K + CH_2Bz{\cdot}CH_2{\cdot}CO_2K.$$

The benzoic acid was separated from the β-benzoylpropionic acid (m. p. 116°. Found, C=67·33; H=5·76. Calc., C=67·41; H=5·61 per cent.) by treatment with light petroleum, in which the latter acid is almost insoluble.

Attempts to prepare β-dibenzoylpropionic acid from the ethyl ester have been unsuccessful.

s-*Tetrabenzoylethane*, $CHBz_2{\cdot}CHBz_2$.

A solution of 10 grams of phenyl α-hydroxystyryl ketone in absolute ether was added to 1 gram of finely divided sodium. After twenty-four hours a solution of 6 grams of iodine in absolute ether was added. The ethereal solution was washed with a solution of sulphurous acid, then with water, dried, and evaporated. The crystalline residue was separated by ethyl alcohol into (i) s-*tetrabenzoylethane*, which is almost insoluble in alcohol, but crystallises from acetone in rhombic plates melting at 205°:

0·2 gave 0·5912 CO_2 and 0·0902 H_2O. C=80·61; H=5·04.

$C_{30}H_{22}O_4$ requires C=80·71; H=4·93 per cent.

(ii) An easily soluble portion, which contained a trace of phenyl α-hydroxystyryl ketone and 0·5 gram of *dibenzoyliodomethane*, $CHIBz_2$, which crystallises from light petroleum in colourless plates melting at 107°:

0·2016 gave 0·1356 AgI. I=36·34.

$C_{15}H_{11}O_2I$ requires I=36·22 per cent.

Dibenzoyliodomethane and s-tetrabenzoylethane reacted with ferric chloride to give a reddish-brown coloration on keeping, more quickly when warmed; and with an alcoholic solution of copper acetate to give pale green, crystalline precipitates after several hours.

Dibenzoylphenylethane, $CHBz_2{\cdot}CH_2Ph$.

An alcoholic solution of benzyl iodide (prepared by heating a mixture of 7·5 grams of benzyl chloride, 10 grams of potassium iodide, and 50 c.c. of absolute alcohol for thirty minutes and filtering from the potassium chloride) was added to a suspension of the sodium derivative of phenyl α-hydroxystyryl ketone (from 11·2 grams of the α-hydroxy-compound and 1·1 grams of sodium) in 50 c.c. of absolute alcohol. The sodium compound dissolved after shaking for several minutes. The solution was poured into water and extracted with ether. The washed and dried ethereal solution was evaporated, and gave a crystalline product, which separated from alcohol in glistening, colourless prisms melting at 108°:

0·202 gave 0·6222 CO_2 and 0·1064 H_2O. C=84·00; H=5·85.

$C_{22}H_{18}O_2$ requires C=84·07; H=5·73 per cent.

That this substance is dibenzoylphenylethane was confirmed by its decomposition by an alcoholic solution of sodium hydroxide to benzoic acid and benzylacetophenone, $CH_2Bz{\cdot}CH_2Ph$ (m. p. 72°). (Found, C=85·69; H=6·84. Calc., C=85·71; H=6·66 per cent.)

If benzyl chloride is used in the above preparation, only the decomposition products are obtained.

Tribenzoylmethane (*α- or diketo-enolic form*), $CBz_2{:}CPh{\cdot}OH$.

Five grams of phenyl α-hydroxystyryl ketone were added to a suspension of 0·5 gram of sodium in absolute ether. On the following day 5 grams of benzoyl chloride were added, and the mixture was heated for several hours. Water was then added, and the solutions were separated.

The ethereal solution on evaporation gave a small quantity of tribenzoylmethane (triketo-form), $CHBz_3$.

The aqueous solution, when acidified with hydrochloric acid and extracted with ether, gave a little benzoic acid and a quantity of dense, colourless crystals melting at 210—226°, which were identified as the diketo-enolic form of tribenzoylmethane. The crystals dissolved in a small quantity of warm alcohol, but almost immediately separated again in the triketo-form as needles melting at 224—226°, which required a much larger volume of boiling alcohol for solution.

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CIII.—*Derivatives of Phenyl Styryl Ketone. Part I. The Tautomeric Forms of Dibenzoylmethane.*

By Robert Duncombe Abell.

When Ruhemann and Watson (Trans., 1904, **85**, 456) showed that Wislicenus's "dibenzoylmethane" is phenyl α-ethoxystyryl ketone, $OEt{\cdot}CPh{:}CH{\cdot}COPh$, the author had been engaged for some time on the repetition of the work of Wislicenus and his pupils on "The Isomeric Forms of Dibenzoylmethane" (*Annalen*, 1899, **308**, 219), and having made several observations not recorded by them or by Sluiter (*Rec. trav. chim.*, 1905, [ii], **24**, 368), the work was continued. This account of the work has been delayed by the tediousness of some of the separations, and by the very limited time which could be given to it.

Phenyl styryl ketone, CHPh:CH·COPh, combines with bromine to form two isomeric dibromides, CHPhBr·CHBr·COPh; the one, crystallising in prisms (m. p. 158°: Claisen and Claparède, *Ber.*, 1881, **14**, 2464), was made use of by Wislicenus (*loc. cit.*); the other crystallises in glistening, flattened prisms, which melt at 122—123°, and can be obtained pure only with difficulty. Miss Smedley (Proc., 1909, **25**, 259) gave 112—113°; Pond, Yorke, and Moore (*Amer. Chem. J.*, 1901, **23**, 789) gave 108—109° as the melting point of this isomeride.*

The dibromide, melting at 158°, reacts with an excess of potassium acetate (Wislicenus, *loc. cit.*, p. 226, gives equimolecular quantities) to form phenyl α-bromostyryl ketone, CPhBr:CH·COPh, which combines with hydrogen bromide to give a 90 per cent. yield of the isomeric dibromide melting at 122°.

In his account of the reaction of phenyl α-bromostyryl ketone with sodium hydroxide, Wislicenus states (*loc. cit.*, p. 227): "Durch halbstündiges Erwärmen mit der weingeistigen Lösung von einem Molekül Aetznatron auf dem Wasserbade wird es *quantitativ* in die Verbindung $C_{15}H_{12}O_2$ übergeführt, die direkt das fast reine neue Isomere ist, indessen sicher eine kleine Menge des alten 'Dibenzoylmethans' [phenyl α-hydroxystyryl ketone] enthält, da die alkoholische Lösung durch Eisenchlorid sofort ziemlich intensiv gefärbt wird." Further, Sluiter (*Rec. trac. chim.*, 1905, [ii], **24**, 368) states that 96 per cent. or more concentrated alcohol is necessary for this reaction.

Equimolecular quantities of phenyl α-bromostyryl ketone and sodium hydroxide in absolute or in 70 per cent. alcohol, when warmed until the alkaline reaction just disappeared, gave: phenyl α-hydroxystyryl ketone, OEt·CPh:CH·COPh (Wislicenus's supposed "Dibenzoylmethane"), and phenyl styryl ketone, CHPh:CH·COPh. Phenyl α-hydroxystyryl ketone, OH·CPh:CH·COPh, is formed only by prolonged heating or by excess of alkali.

The formation of phenyl styryl ketone, which was not recognised by Wislicenus, Ruhemann and Watson, Miss Smedley (Trans., 1910, **97**, 1490), or Sluiter, seems to depend on the presence of water. Certainly it was formed in greatest quantity in 70 per cent. alcohol, and when sodium ethoxide in absolute alcohol was used (this vol., p. 993) the amount of phenyl styryl ketone was so small as to be scarcely recognisable.

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* This isomeride was isolated by the author in Nov., 1902. Until a short time ago, the author was not aware of the work of Pond, Yorke, and Moore.

EXPERIMENTAL.

Phenyl Styryl Ketone, CHPh:CH·COPh.

An improved yield (90 per cent.) of the substance was obtained by modifying Claisen's method (*Ber.*, 1887, **20**, 665) by using 48 grams of benzaldehyde, 48 grams of acetophenone, and 12 c.c. of a 20 per cent. solution of sodium methoxide in methyl alcohol.*

The Isomeric Phenyl Styryl Ketone Dibromides, CHPhBr·CHBr·COPh.

By adding bromine (1 mol.) to a solution of phenyl styryl ketone (1 mol.) in chloroform, and crystallising the product from alcohol, Claisen and Claparède (*loc. cit.*) obtained the dibromide melting at 156—157°, and from the alcoholic mother liquors Pond, Yorke, and Moore (*loc. cit.*) obtained the dibromide melting at 108—109° (Miss Smedley gives 112—113°).

The author finds that the former of these dibromides crystallises from alcohol in white tufts of prisms, or from a mixture of alcohol and carbon disulphide in clusters of dense prisms which melt at 158°. The latter isomeride crystallises in glistening, colourless, flattened prisms, which melt at 122—123°, and readily turn yellow on exposure to sunlight. (Found, Br = 43·45. Calc., Br = 43·47 per cent.)

Separation of the Isomeric Dibromides.

Simple recrystallisation from alcohol gives a mixture of the dibromides which melts at 112—113°, and which may be mistaken for one of the pure substances (compare Miss Smedley, *loc. cit.*).

The isomeride melting at 122° can be obtained pure as follows: The alcoholic mother liquors are concentrated by distillation, a small quantity of carbon disulphide is added, the hot solution is filtered, heated to boiling, and set aside to crystallise slowly. On the following day an examination of the crystals which have separated on the bottom of the flask will show two forms. The solution is heated until the colourless crystals dissolve, filtered, heated to boiling, and again set aside for slow crystallisation to take place. The operation is repeated until separation is complete.

With suitable apparatus and careful work little or no material is lost, but the complete separation takes several months; thus in one case the first crop of crystals of the isomeride melting at 122°

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* One of the products of this reaction, if allowed to come into contact with the skin, causes itching and redness, followed by an eruption similar to eczema, which is very painful while it lasts.

was obtained only after daily crystallisation for upwards of three months, and the complete separation of the isomerides required six months of the above treatment.

Ruhemann and Watson (*loc. cit.*), who did not recognise this isomeride, recommend the bromination of phenyl styryl ketone in carbon disulphide in place of chloroform as giving a better yield of the dibromide melting at 158°. Comparative brominations of 10 grams of phenyl styryl ketone in 25 c.c. of each of these solvents gave:

	In carbon disulphide.		In chloroform.	
	Grams.	Per cent. of theory.	Grams.	Per cent. of theory.
Yield of m. p. 158°	16·63	94·0	16·12	91·1
,, ,, 122°	1·01	5·7	1·4	7·9
Total yield	17·64	99·7	17·52	99·0

The total yield of dibromide and the yield of the isomeride melting at 158° is slightly better in carbon disulphide solution. Chloroform favours to a small extent the formation of the isomeride melting at 122°. The chief advantage of the use of carbon disulphide is that after preparation in this medium the isomerides are more easily separated by subsequent recrystallisation than when chloroform is used.

Preparation of the Dibromide melting at 122°.

The best means of preparing this substance is from phenyl α-bromostyryl ketone, CPhBr⁚CH·COPh (p. 1002), which unites with hydrogen bromide in carbon disulphide or chloroform solution. Here the influence of the solvent is much more marked than above.

Comparative reactions with 10 grams of phenyl α-bromostyryl ketone in 50 c.c. of the respective solvents when treated with dry hydrogen bromide until the theoretical quantity had been absorbed gave:

	In carbon disulphide.		In chloroform.	
	Grams.	Per cent. of theory.	Grams.	Per cent. of theory.
Yield of m. p. 158°	1·29	10·0	3·82	29·8
,, ,, 122°	11·51	89·8	8·73	68·0
Total yield	12·80	99·8	12·55	97·8

The carbon disulphide undoubtedly favours the formation of the dibromide melting at 122°. Further, it was noticed that hydrogen bromide was taken up much more slowly in carbon disulphide solution, and that the dibromides were more easily separated than when prepared in chloroform solution.

The mixture of dibromides was separated as indicated above.

Phenyl α-Bromostyryl Ketone, CPhBr:CH·COPh.

Wislicenus (*loc. cit.*, p. 226) describes this substance as a yellow oil boiling without decomposition at 232—234°/12 mm., melting at 43—44°, and obtained by boiling phenyl styryl ketone dibromide (m. p. 158°: 1 mol.) with an alcoholic solution of potassium acetate (1 mol.) for several hours.

The author's experience is that equimolecular quantities of the reacting substances always gave a red-coloured oil, which underwent very considerable decomposition when distilled, and in some cases only a small portion of the distillate crystallised.*

An almost quantitative yield was obtained by boiling a solution of 75 grams of the dibromide melting at 158° and 25 grams of anhydrous potassium acetate (theory = 20 grams) in 1 litre of 95 per cent. alcohol for three to four hours. The alcohol was rapidly evaporated, and the residue dissolved in ether and water. The ethereal solution was washed, dried, and distilled. The yellow, viscid oil so obtained boiled at 230—231°/18 mm. [218°/12 mm.] without decomposition or discoloration, and rapidly became crystalline. The yellow, crystalline mass was crushed and allowed to remain for several hours in contact with light petroleum (b. p. 40—50°), the whole filtered, and the residue well washed with the same solvent; it then melted at 43—44°. The small quantity of oil which was removed by the light petroleum was purified by redistillation.

Behaviour of Phenyl α-Bromostyryl Ketone with Alcoholic Sodium Hydroxide.

According to Wislicenus (*loc. cit.*, p. 227) an alcoholic solution of equimolecular quantities of phenyl α-bromostyryl ketone and sodium hydroxide when warmed for half an hour on the water-bath gave "dibenzoylmethane" and a trace of phenyl α-hydroxystyryl ketone.

On repeating this work, a solution of 4 grams of sodium hydroxide and 28·7 grams of the α-bromo-compound in 500 c.c. of 95 per cent. alcohol, when heated to boiling for half an hour, gave phenyl styryl ketone and its α-hydroxy- and α-ethoxy-derivatives, OH·CPh:CH·COPh and OEt·CPh:CH·COPh respectively, which were isolated and identified as follows:

The reaction mixture, being still alkaline, was saturated with carbon dioxide and filtered. The alcohol was rapidly distilled from the filtrate, and the residue was dissolved in ether and water. The washed ethereal solution was distilled, and the residual oil, when treated with an alcoholic solution of copper acetate, gave 8 grams of the copper derivative of phenyl α-hydroxystyryl ketone (=7 grams of α-hydroxy-compound). The alcoholic filtrate was again distilled, and the residue dissolved in ether and water. The washed and dried ethereal solution contained an oil which distilled at 240—250°/40 mm. and became partly crystalline. After removing the oil by means of a porous plate, the solid portion crystallised from light petroleum in prisms melting at 77·5—78°, and was identified as phenyl α-ethoxystyryl ketone (compare Ruhemann and Watson, *loc. cit.*, and Sluiter, *loc. cit.*) by its properties and by analysis. (Found, C=80·89; H=6·43. Calc., C=80·95; H=6·35 per cent.)

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* This was confirmed by Dr. Crowther (private communication), who obtained one preparation of more than 100 grams, which he kindly gave to me; the substance id not crystallise during the six years that it was kept.

The oil extracted from the porous plate by means of ether was redistilled, and as it did not crystallise, was brominated in carbon disulphide solution. The product, which was wholly crystalline, was recrystallised from ethyl alcohol, and gave:

(i) Dibenzoylbromomethane, $CHBrBz_2$ (prisms, m. p. 92°), and (ii) phenyl styryl ketone dibromide (white prisms, m. p. 158°), the relative quantities of which indicated that the oil consisted almost entirely of phenyl styryl ketone mixed with a small amount of its α-ethoxy-derivative, from which it was not possible to separate it by distillation.

In other reactions where a slight excess of sodium hydroxide was used, the yield of phenyl α-hydroxystyryl ketone was increased at the expense of its ethyl ether.

Further, in consequence of Sluiter's statement (*loc. cit.*) that 96 per cent. or more concentrated alcohol must be used in this reaction, and of the present author's own observation in other preparations of the ethyl ether that prolonged heating partly hydrolysis it, two experiments were made, namely, one in absolute alcohol (28·7 grams of phenyl α-bromostyryl ketone with 143 c.c. of an absolute alcoholic solution of sodium hydroxide, 1 c.c.=0·028 gram NaOH), the other in 70 per cent. alcohol (14·4 grams of the α-bromo-compound with 77 c.c. of a solution of sodium hydroxide in 70 per cent. alcohol; 1 c.c.=0·026 gram NaOH).

The mixtures were heated until the alkaline reaction just disappeared, then precipitated with water, and worked up as above. Phenyl styryl ketone and its α-ethoxy-compound were formed in both cases. Phenyl α-hydroxystyryl ketone was not formed in either case. The presence of water certainly caused a decrease in the yield of phenyl α-ethoxystyryl ketone, and an increased yield of phenyl styryl ketone.

In conclusion, the author desires to direct attention to the fact that the diketone, dibenzoylmethane, CH_2Bz_2, has not yet been isolated. The "dibenzoylmethane" of Claisen (*Annalen*, 1896, **291**, 52; *Ber.*, 1887, **20**, 655; 1905, **38**, 693) and of Baeyer and Perkin (*Ber.*, 1883, **16**, 2134; Trans., 1885, **47**, 253) is, as was pointed out by Wislicenus (*loc. cit.*), phenyl α-hydroxystyryl ketone, OH·CPh⁚CH·COPh, the keto-enolic form of the 1 : 3-diketone. This is confirmed by the work of Miss Smedley (Trans., 1910, **97**, 1493) and K. Meyer (*Annalen*, 1911, **380**, 212–242).

The diketone being unknown, its tautomeride,

OH·CPh⁚CH·COPh,

which is probably the most stable 1 : 3-keto-enolic compound known at the present time, should not be referred to in current literature as "dibenzoylmethane."

The "dibenzoylmethane" of Wislicenus (*loc. cit.*) is the ethyl ether of phenyl α-hydroxystyryl ketone, OEt·CPh⁚CH·COPh.

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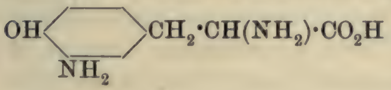
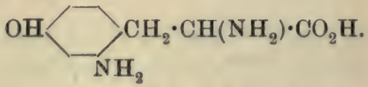
CIV.—*The Constitution of Aminotyrosine and the Action of Oxydases on Some Tyrosine Derivatives.*

By CASIMIR FUNK.

IN connexion with the synthesis of *dl*-3 : 4-dihydroxyphenylalanine (Trans., 1911, **99**, 554), an attempt was made to obtain the optically active compound by employing aminotyrosine, which was considered by Neuberg to be 3-aminotyrosine ("Handbuch der Biochemie," Oppenheimer, Vol. 4, Part II., p. 363). An analogous process was used by Erlenmeyer and Lipp (*Annalen*, 1883, **219**, 166) in the preparation of tyrosine from aminophenylalanine. Aminotyrosine was prepared according to the methods described by Strecker (*Annalen*, 1850, **73**, 70), Staedeler (*ibid.*, 1860, **116**, 57), and Beyer (*Zeitsch. Chem.*, 1867, 437) from tyrosine through the nitro-compound. In these papers very few experimental data, no melting points, reactions, or analyses were given. The tyrosine employed for the synthesis was optically active *l*-tyrosine, but both the nitro- and amino-tyrosine obtained were completely inactive, so that racemisation must have occurred during the preparation of the nitro-compound. By diazotising the aminotyrosine according to Erlenmeyer and Lipp's method, no 3 : 4-dihydroxyphenylalanine was obtained, but a substance was isolated which possessed the composition of the initial product, differing, however, from the latter by its resistance to oxidation, and especially to the action of oxydases. Bertrand (*Bull. Soc. chim.*, 1896, [iii], **15**, 791) has shown that these ferments are only able to oxidise ortho- and para-compounds. It must be concluded, therefore, that the new non-oxidisable aminotyrosine is a meta-compound, and that the original nitro- and amino-tyrosine are mixtures of two isomerides. namely, the ortho- and meta-compounds:



and



By the action of nitrous acid, 3-aminotyrosine is destroyed and 2-aminotyrosine, described above, left in the solution.

Until recent times the belief was current that the ferments laccase and tyrosinase were specific in their action; thus laccase was considered to oxidise only phenols and aminophenols, tyrosinase only tyrosine. It has, however, since been shown that this is not the case, and in the present paper further proof of this is given, and it is shown that 3:4-dihydroxyphenylalanine, aminotyrosine, and adrenaline are oxidised equally well by both ferments.

The action of laccase and tyrosinase might be used with good results for the determination of the position of hydroxy- and amino-groups in compounds, analogous to those described in this paper.

EXPERIMENTAL.

Preparation of Nitrotyrosine.

l-Tyrosine (150 grams) from silk was suspended in water, and nitric acid (600 c.c.; D 1·3) was added drop by drop, the mixture being kept cool in cold water and continually stirred with a turbine. During the reaction the nitrate of the nitrotyrosine separated in golden-yellow needles (130 grams), which melted and decomposed at 170°. The crystals were dissolved in a little water, ammonia was added, and the solution was evaporated on the water-bath until crystals began to separate. Nitrotyrosine was thus obtained in yellow needles, which after drying under diminished pressure at 110°, melted at 220°, and were optically inactive. Yield, 104 grams.

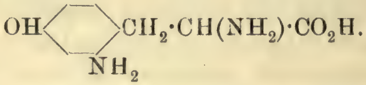
Preparation of Aminotyrosine.

Nitrotyrosine (104 grams) was dissolved in water and heated on the water-bath for one hour with tin (200 grams) and hydrochloric acid (1200 c.c.; 4:10). The warm solution was then decanted, freed from tin by means of hydrogen sulphide, and the filtrate evaporated under diminished pressure in a stream of coal-gas. Colourless needles of dichloroaminotyrosine separated out, which melted at 155—160°. The hydrochloride was dissolved in a very little water, and neutralised with the calculated amount of 2*N*-potassium hydroxide. On evaporation under diminished pressure, aminotyrosine (60 grams) was obtained, which on recrystallisation from water gave slightly grey-coloured prisms melting and decomposing at 265°. This compound gave with ferric chloride a pink coloration, and with Millon's reagent first an orange coloration, followed by reduction of the mercury salt. The aqueous solution assumes a pink colour after a short time. The substance is optically inactive:

0·233, by Kjeldahl's method, required 23·6 c.c. $N/10\text{-}H_2SO_4$. $N = 14·18$.

$C_9H_{12}O_3N_2$ requires $N = 14·28$ per cent.

Preparation of 2-Aminotyrosine,



$$OH\langle\;\rangle CH_2\cdot CH(NH_2)\cdot CO_2H. \quad (NH_2)$$

A solution of aminotyrosine (10 grams in molecular proportions of sulphuric acid) kept at −2° was treated with a slow stream of gaseous nitrous acid, prepared from 3·6 grams of sodium nitrite dissolved in 50 c.c. of water and 5·1 grams of sulphuric acid in 50 c.c. of water. The solution was then boiled for one hour, during which time a little nitrogen was evolved. After the removal of sulphuric acid by means of barium hydroxide, the solution was evaporated under diminished pressure. The residue yielded 5 grams of yellow needles, which after recrystallisation from water and drying under diminished pressure at 110° melted at 273°. With ferric chloride a pink coloration and with Millon's reagent a white precipitate were obtained. The aqueous solution was not oxidised on contact with air:

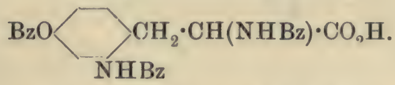
0·2074 gave 0·4188 CO_2 and 0·1122 H_2O. $C = 55·07$; $H = 6·01$.

0·1868, by Kjeldahl's method, required 18·6 c.c. $N/10\text{-}H_2SO_4$. $N = 13·99$.

$C_9H_{12}O_3N_2$ requires $C = 55·06$; $H = 6·17$; $N = 14·28$ per cent.

This substance is aminotyrosine, and differs from the initial product by the melting point, stability against oxidation, the colour of the crystals, and, as is shown later, in its behaviour towards oxydases. From the latter point of view the substance must be considered to be 2-*aminotyrosine.* The mixture of both substances melted at 260°.

Tribenzoyl-2-aminotyrosine,



Aminotyrosine (0·5 gram) was dissolved in *N*-potassium hydroxide (5·1 c.c.); to this solution sodium hydrogen carbonate (3·5 grams) was added, and then benzoyl chloride (2·3 grams) in small portions at a time. The compound separated out during the reaction as the sodium salt. It was then treated with dilute sulphuric acid, the precipitate finally extracted with light petroleum to dissolve the benzoic acid, and recrystallised from a mixture of acetic acid and ethyl acetate. Colourless, microscopical needles (0·9 gram) were obtained, which were sparingly soluble in alcohol or ethyl acetate, readily so in acetic acid, and insoluble in water. After drying under diminished pressure at 100°, they melted and decomposed at 192—195°:

0·1766 gave 0·4602 CO_2 and 0·0746 H_2O. $C=71{\cdot}07$; $H=4{\cdot}69$.

$C_{30}H_{24}O_6N_2$ requires $C=70{\cdot}83$; $H=4{\cdot}76$ per cent.

An attempt was then made to separate the mixture in the initial product by means of benzoylation, but was unsuccessful. Three grams of the initial aminotyrosine yielded only 0·3 gram of a benzoyl compound which melted at 191—195°, whilst in the mother liquor no further product could be detected. By mixing both benzoyl compounds, the melting point was not depressed.

Action of Laccase and Tyrosinase.

For these experiments 0·05 gram of each substance was dissolved in 5 c.c. of water, and 1 c.c. of the ferment solution added. The tyrosinase was prepared from *Agaricus campestris*, and the laccase from the latex tree (*Rhus succedanea*). The colorations were

	Laccase.	Tyrosinase.
Quinol	red	no change
Tyrosine	no change	black
Aminotyrosine	black	black
2-Aminotyrosine	no change	no change
3 : 4-Dihydroxyphenylalanine	pink	pink
dl-Adrenaline	pink	pink
Nitrotyrosine	no change	no change

observed after five minutes. The experiments with quinol and tyrosine showed that the laccase was free from tyrosinase and the tyrosinase free from laccase.

The difference between the aminotyrosines is thus evident. These experiments also reveal the new fact that many substances are oxidised both by laccase and tyrosinase.

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CV.—*The Viscosity of Compounds Containing Tervalent Nitrogen. Part I. The Amines.*

By ALBERT GEORGE MUSSELL, FERDINAND BERNARD THOLE, and ALBERT ERNEST DUNSTAN.

IN view of the importance of considering critically the evidence brought forward from a variety of physical properties in questions of chemical constitution, it has been thought desirable to extend further the work already published on the viscosity of the amides (Dunstan and Mussell, Trans., 1910, **97**, 1935), particularly since an important contribution to the subject has appeared, based on molecular surface energy (Turner and Merry, Trans., 1910, **97**, 2081).

The results obtained from both investigations led to the same conclusions:

(1) That the amides were associated to a considerable extent.

(2) That replacement of amidic hydrogen by alkyl groups depressed the association.

(3) That the aromatic amides were strongly associated, although as a general rule compounds containing the aryl groups are less associated than those of the aliphatic type.

(4) That the association of the amides is not due to any hydroxylic structure.

Turner and his collaborators adhere to the view that the whole problem of association is intimately bound up with that of the electrical state of the molecule, since they have shown that there is a general connexion between the degree of association and the dielectric constant (see also Walden, *Zeitsch. physikal. Chem.*, 1910, **70**, 569, and Trans., 1908, **93**, 876; 1910, **97**, 1605; 1911, **99**, 685). On the other hand, the present authors are of opinion that since all evidence for association is gained by the study of physical properties, such as surface tension and viscosity, and since undoubtedly the association is caused by the presence of a centre of unsaturation in the molecule, it is of increasing importance to investigate the effects on physical properties in general of such unsaturated groupings.

In a series of papers, of which Part I. has recently appeared (Hilditch and Dunstan, *Zeitsch. Elektrochem.*, 1911, **17**, 929), the effects of unsaturation are being studied in some detail. It appears to be certain that not only does an unsaturated grouping raise the values of boiling point, melting point, optical rotation, refractivity, and viscosity, but that a further and more considerable enhancement is brought about when two or more of such centres of residual chemical energy are adjacent. Now in the aliphatic amides there are two such centres, and in the aromatic, three. It is not surprising, then, that benzamide and acetanilide show evidence of association.

At the same time, however, it has become increasingly evident to the authors that there are three modifying factors at work, tending fundamentally to affect the numerical values of all physical properties which possess considerable constitutive tendencies, and these are symmetry, association, and conjugation,* although perhaps association in many cases is a direct consequence of such conjugation.

When the value of the association factor and $\frac{\eta \times 10^6}{\text{Mol. vol.}}$ are compared for the amides, it will be obvious that there is a general connexion between them, since an increase in association factor is accompanied by enhanced values for $\frac{\eta \times 10^6}{\text{Mol. vol.}}$; but where the amidic hydrogen is entirely replaced, as, for example, in methylacetanilide, then both association factor and viscosity suffer a considerable decrease.

Turning to the amines, Turner and Merry drew the following conclusions from the molecular surface energies of nine of those compounds:

(1) Primary amines are slightly associated; the secondary and tertiary amines are non-associated (in the liquid state).

(2) The following amines gives abnormally high values of K and low values of x—tripropylamine, triamylamine, diphenylamine, dibenzylamine, and tribenzylamine.

Although not specifically stated by Turner and Merry, aniline is more associated than amylamine, the fatty compound of nearest molecular weight.

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* Using the term conjugation merely to express propinquity of centres of unsaturation.

These results will be discussed in the proper place in the sequel. In the present paper the viscosity has been determined for forty-four amines in the liquid or fused condition. Further, solutions have been examined both in amyl acetate* (see Thole, Trans., 1910, **97**, 2600) and in *N*-hydrochloric acid. The choice of the latter solvent will be obvious when one considers that in such solutions tertiary nitrogen becomes quinquevalent; therefore, any conjugation effect is destroyed, and further, that Turner has shown that in aqueous solution amines are not associated (Trans., 1911, **99**, 695). It may be pointed out at once that all the amines examined gave values in acid solution which were almost identical, so that these numbers will not be referred to further.

EXPERIMENTAL.

The apparatus used and the precautions to be observed have been described in previous papers (see Trans., 1910, **97**, 1940 for high temperature work). The amines were partly purchased from Schuchardt; some, however, were specially prepared. β-Phenylethylamine was prepared from phenylacetonitrile, and purified by precipitation as carbonate; α-phenylethylamine by Tafel's method from acetophenonephenylhydrazone, and γ-phenylpropylamine by Tafel's method from cinnamaldehydephenylhydrazone. *ac-* and *ar*-Tetrahydro-β-naphthylamines were prepared according to Bamberger's method. The liquid amines were distilled after contact with potassium hydroxide; the solid compounds were recrystallised from an appropriate solvent and distilled. As a general rule, the substances were distilled directly into the viscometer to avoid any trouble from suspended dust particles.

The results for the pure liquids and the fused amines are set out in terms of the expression $\frac{\eta \times 10^6}{\text{Mol. vol.}}$, and those for the solutions in amyl acetate and in *N*-hydrochloric acid in terms of the viscosity at the equivalent concentration $\frac{\text{Mol. wt.}}{10}$ per cent.

The values of the expression $\frac{\eta \times 10^6}{\text{Mol. vol.}}$ have been shown (Dunstan and Thole, *J. Chim. phys.*, 1909, **7**, 204) to give some indications as to the degree of molecular complexity; for example, the fatty esters, ketones, and alkyl halides give numbers ranging between 40 and 70, whereas water has the value 500 and glycol 2750. As an illustration of the utility of the expression, associated phenol has a molecular viscosity of 453, whilst that for the closely related unassociated anisole is 66·6.

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* The results for the amyl acetate solutions are not referred to further, since they lead to precisely the same conclusions as those for the liquids themselves.

TABLE I.

Aliphatic Amines at 25°.

Amine.	D^{25}_4.	Viscosity.	$\frac{\eta \times 10^6}{\text{Mol. vol.}}$
n-Propylamine	0·715	0·00353	42·9
Allylamine	0·762	0·003745	50·0
n-Butylamine	0·759	0·00681	70·8
*iso*Butylamine	0·749	0·00553	56·8
*iso*Amylamine	0·757	0·007235	63·0
Diethylamine	0·700	0·00367	36·2
Di*iso*butylamine	0·751	0·00687	40·0
Triethylamine	0·725	0·00363	26·1

From the above results it follows that primary amines have the highest value for $\frac{\eta \times 10^6}{\text{Mol. vol.}}$, followed by the secondary, and lastly, the tertiary compounds. The value for $\frac{\eta \times 10^6}{\text{Mol. vol.}}$ rises with increasing molecular weight.

Iso-compounds have a lower viscosity than the isomeric normal amines, a further illustration of the general rule that increased symmetry causes decreased viscosity. The large values for the association factors in the fatty amines goes *pari passu* with the increased value for $\frac{\eta \times 10^6}{\text{Mol. vol.}}$, whilst in the secondary and tertiary series Turner's work shows that so far from there being any association there is an abnormally high value for K and a correspondingly low association factor:

Temperature 20—30°.

Amine.	K.	x.
n-Propylamine	1·83	1·24
Dipropylamine	2·28	0·90
Tripropylamine	2·5	0·78

	$\frac{\eta \times 10^6}{\text{Mol. vol.}}$
*iso*Butylamine	56·8
Di*iso*butylamine ...	40·0
Diethylamine	36·2
Triethylamine	26·1

In considering the disturbing influences at work on both sets of results, effects due to internal conjugation can be omitted, but it is a very open question whether the whole problem of association is not due to the external influence of each molecule on its neighbours. There remains, then, the effect of increased symmetry due to the replacement of hydrogen by alkyl groups. Turner and Merry (*loc. cit.*) point out that a variety of compounds shows also an abnormal value for K, and incline to the view that the reason lies in increased molecular weight.

The result for allylamine is interesting, since the value for $\frac{\eta \times 10^6}{\text{Mol. vol.}}$ is markedly higher than that of propylamine. Recently Hilditch and Dunstan (*Zeitsch. Elektrochem.*, 1911, **17**, 929) have examined a large number of cases of conjugated unsaturation of the type exhibited by allylamine, and invariably found it to be connected with general enhancement of boiling point, melting point, viscosity, refractivity, and optical rotatory power.

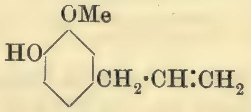
TABLE II.

Aromatic Amines at 25° *and* 130°.

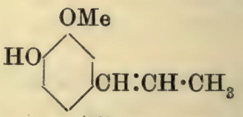
Amine.	D_4^{25}.	η_{25}.	$\frac{\eta_{25} \times 10^6}{\text{Mol. vol.}}$	η_{130}.	$\frac{\eta_{130} \times 10^6}{\text{Mol. vol.}}$.
Aniline	1·022	0·0362	398	0·00555	55·5
Methylaniline	0·984	0·0202	185	—	—
Dimethylaniline	0·954	0·01285	101	—	—
Ethylaniline	0·958	0·0204	162	—	—
Diethylaniline	0·933	0·0195	123·5	—	—
o-Toluidine	0·997	0·0376	351	0·00550	46·2
m-Toluidine	0·987	0·03315	306	0·00506	42·0
p-Toluidine	—	—	—	0·00522	43·3
Ethyl *o*-toluidine	0·948	0·0198	139	—	—
Ethyl *p*-toluidine	0·942	0·0240	167	—	—
Aniline	—	—	—	0·00555	55·5
Acetanilide	—	—	—	0·0190	142·0
Methylacetanilide *	—	—	—	0·00818	53·6

* Dunstan and Mussell at 102° (*loc. cit.*).

In discussing the numbers for the aromatic amines at 25°, one is struck with the increase in viscosity in passing from the fatty series. The high value for aniline is paralleled by that of phenol (Thole, *loc. cit.*). In each case there is a group capable of association, possessing considerable residual affinity, and it is adjacent to the phenyl residue. Hence, to the effect of association is added that of conjugation. The effect of this superposition of unsaturation is excellently illustrated by the molecular viscosities of eugenol, *iso*eugenol, safrole, and *iso*safrole:



448·5.



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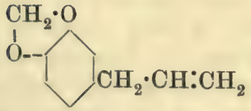

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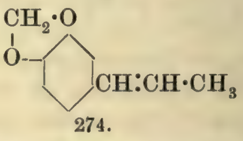


274.

The characteristic fall in molecular viscosity from primary, secondary, to tertiary exhibited by the alkylanilines is clearly a further example of what was found to hold good in the fatty series. Highly interesting is the change from aniline to acetanilide, where the change from primary to secondary character is accompanied by an increase in viscosity. It must not be forgotten, however, that here is a case of double conjugation, for the nitrogen is now connected with two unsaturated groupings, the phenyl and the acyl. In the case of methylacetanilide the replacement of hydrogen by an alkyl group has the customary effect in depressing the viscosity:

Amine.		*K*.	*x*.	$\frac{\eta \times 10^6}{\text{Mol. vol.}}$ 130°.
Aniline	(45— 75°)	2·0	1·09	55·5
Acetanilide	(120—130)	1·87	1·21	142·0
Methylacetanilide..	(120—130)	2·24	0·92	53·6 (120°)

It scarcely seems necessary to adopt the view that the increased values of *K* are due only to increased molecular mass, since the trifling increment of a methyl group would not account for the change in *K* and *x* shown above; but seeing that the association factor and the viscosity run parallel, it is best to look for some underlying cause, namely, the change in condition of the nitrogen atom. Broadly, then, it appears that aniline is more associated than the fatty amines of corresponding molecular weight; that replacement of hydrogen by alkyl groups depresses the viscosity, but substitution of an acyl group for hydrogen increases both viscosity and the association factor.

TABLE III.

Nucleus Amines at 25°.

Amine.	D^{25}_{4}.	η_{25}.	$\frac{\eta \times 10^6}{\text{Mol. vol.}}$
Pyridine	0·978	0·00878	109
Piperidine	0·880	0·0216	166
Quinoline	1·090	0·0337	285
*iso*Quinoline	1·096	0·0357	305
Tetrahydroquinoline..	1·067	0·05255	421

Ramsay and Shields (*loc. cit.*, p. 1101) found for pyridine and quinoline values of *K* slightly in excess of the average, 2·121, so that no association is evident, but piperidine has a value $x = 1{\cdot}08$ (16·5—46·2°):

	K.	*x*.	$\frac{\eta \times 10^6}{\text{Mol. vol.}}$
Pyridine	2·226	0·93	108·6
Piperidine..................	2·062	1·08	166·0

Hence, even when the nitrogen atom is part of a ring system the agreement pointed out in the previous series holds good. The viscosities of the tertiary nucleus amines are midway between those of the aromatic and aliphatic compounds. It is noteworthy that the influence of ring-formation is very considerable, seeing that the molecular viscosities of piperidine, diethylamine, and *iso*amylamine are respectively 166, 36·2, and 63, whilst their molecular weights are of the same order. The difference between quinoline and *iso*quinoline is interesting; perhaps one might regard the nitrogen atom in quinoline as affected by the phenyl nucleus adjacent to it to a greater extent than in *iso*quinoline.

Tetrahydroquinoline evidently falls into line with piperidine, and illustrates the general observation that a secondary amine has a higher viscosity than a tertiary compound.

TABLE IV.

The Benzylamines and Phenylamines at 25° and 130°.

Amine.	D_4^{25}.	η_{25}.	$\frac{\eta_{25} \times 10^6}{\text{Mol. vol.}}$	K.	η_{130}.	$\frac{\eta_{130} \times 10^6}{\text{Mol. vol.}}$
Aniline …………	1·022	0·0362	398	1·69	0·00555	56·5
Benzylamine ……	0·981	0·0159	146	2·12	0·00442	37·0
Dibenzylamine …	1·019	0·0616	319	2·85	0·00812	39·5
Tribenzylamine …	—	—	—	3·58	0·0209	69·9
Aniline …………	—	—	—	—	0·00555	55·5
Diphenylamine …	—	—	—	—	0·0104	61·1
Triphenylamine …	—	—	—	—	0·0640	262·0
Methyldiphenylamine …………	—	—	—	—	0·00812	41·5
Benzylaniline ……	—	—	—	—	0·01203	64·5
Allylaniline………	—	—	—	—	0·00506	34·2

At first sight the results in the above table contradict what has gone before, seeing that tertiary tribenzylamine and tertiary triphenylamine have far greater viscosities than the primary and secondary compounds. It will be seen, further, that the values for K also increase in the same order; hence the numbers for x might warrant the conclusion that the di- and tri-benzylamines were dissociated. Since both tribenzylamine and triphenylamine are extremely symmetrical compounds, and since it was found that triethylamine—also highly symmetrical—was the least viscous of the fatty amines, it follows that some other factor is overwhelming any lowering of viscosity due to symmetry. This disturbing cause is conjugation. On comparing the three phenylamines with the three benzylamines, it is found that the former compounds have the greater viscosity, for the nitrogen atom is more directly associated with the phenyl group. This is still more clearly seen when the association factors of aniline and benzylamine are contrasted, for whereas the latter substance gives a normal value of K, aniline is distinctly associated. It was shown under the heading of the aromatic amines that the change from acetanilide to methylacetanilide led to an increase in K, but to a diminution both in x and in the molecular viscosity. It is obvious, therefore, that the high values for K and molecular viscosity in the present case cannot be due merely to the substitution for hydrogen of phenyl and benzyl *per se*, but to a specific effect in the group itself, and each group is, in point of fact, a centre of unsaturation.

To clinch this point the case of methyldiphenylamine should be considered; replacement of hydrogen by methyl lowers the viscosity, replacement by phenyl and benzyl raises it. Still further to illustrate this contention, benzylaniline and allylaniline were examined, and it becomes increasingly clear that alkyl groups, when substituted for hydrogen, depress viscosity, whilst phenyl and benzyl groups in similar circumstances raise the viscosity. We propose, then, to explain the anomalous behaviour of the benzylamines and phenylamines, both with respect to viscosity and molecular surface energy as being due to a reinforced type of conjugation.

TABLE V.

The Naphthylamines and the Reduced Naphthylamines at 130°.

	η_{130}.	$\frac{\eta \times 10^6}{\text{Mol. vol.}}$
α-Naphthylamine	0·0144	104·0
Dimethyl-α-naphthylamine	0·00868	48·7
ar-Tetrahydro-α-naphthylamine	0·0118	78·2
β-Naphthylamine	0·0134	91·6
Dimethyl-β-Naphthylamine	0·00952	54·7
ac-Tetrahydro-β-naphthylamine	0·01085	67·0

β-Naphthylamine, being a meta-compound, follows the general rule, and is less viscous than the α-derivative; further, one may regard it as being less influenced by the phenyl group than is the compound. The alkylated derivatives also follow the rule that replacement of hydrogen by alkyl substituents decreases the viscosity, whilst the aromatic reduced naphthylamine has a higher viscosity than the alicyclic, since in the former case the amino-group is still directly coupled with a phenyl nucleus.

TABLE VI.

The Phenyl Substituted Alkyl Amines at 25°.

Amine.	D^{25}.	η_{25}.	$\frac{\eta \times 10^6}{\text{Mol. vol.}}$
Aniline	1·022	0·0362	398
Benzylamine	0·981	0·0159	146
α-Phenylethylamine	0·953	0·0166	131
β-Phenylethylamine	0·972	0·0307	246
γ-Phenylpropylamine	1·008	0·0396	295

The investigation in this series is of a preliminary nature, since further compounds are being prepared for another research. The figures, however, suffice to show that the relative position of the amino- and phenyl groups has a large effect on the viscosity. There is a noticeable fall in viscosity in passing from aniline to benzylamine, and this has been explained in previous pages, but it is not yet certain to what extent these two groups can affect each other spatially.

General Conclusions.

(1) Forty-four amines have been examined in the pure state at 25° and 130° in some cases. Some also were examined in amyl acetate and hydrochloric acid solution.

(2) The order of increasing value for $\frac{\eta \times 10^6}{\text{Mol. vol.}}$ is tertiary—secondary—primary.

(3) Substitution of an alkyl group for hydrogen lowers the value for $\frac{\eta \times 10^6}{\text{Mol. vol.}}$.

(4) Substitution of an acyl, phenyl, or benzyl group for hydrogen increases this value.

(5) Substances with a very high value for K have correspondingly high values for the expression $\frac{\eta \times 10^6}{\text{Mol. vol.}}$.

(6) There is a very close connexion between association constant and viscosity.

(7) Conjugation of unsaturated groups increases both viscosity and K.

PHYSICAL CHEMISTRY LABORATORY,
EAST HAM TECHNICAL COLLEGE.

CVI.—*Electrolytic Reduction. Part VI. Unsaturated Aldehydes and Ketones.*

By HERBERT DRAKE LAW.

THE compounds hitherto submitted to electrolytic reduction have been confined entirely to the aromatic series. Distinct relations have been established, and it has been proved repeatedly that the rate of reduction of aromatic aldehydes and ketones diminishes as the potential of reduction is lowered; thus benzaldehyde is reduced much more readily with lead cathodes than with copper, but at the same time the supertension of lead is much higher than that of copper. It has been shown, further, that the position of substituted groups in the benzene nucleus greatly influences the nature of the reduction product. The significance of the latter relation is not clear, and the present work was undertaken in order to obtain a more intimate knowledge of the reactions taking place. It was hoped that a comparative study of aliphatic and alicyclic ketones and aldehydes would throw a considerable amount of light on the nature of the benzene nucleus. Many compounds were investigated, but the complicated nature of the reduction products rendered it necessary considerably to curtail the scope of the work. The following experiments are confined chiefly to an investigation of the products of reduction of aldehydes and ketones on lead cathodes.

EXPERIMENTAL.

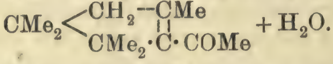
Crotonaldehyde.

The reduction products of crotonaldehyde have been studied previously. The chief substance formed is butyl alcohol. The electrolytic method gave practically the same result in acid medium. Twenty-five grams of crotonaldehyde, 50 c.c. of alcohol, 150 c.c. of water, and 10 grams of sulphuric acid were reduced in the apparatus already described (Trans., 1906, **89**, 1512), but the precaution was taken to close the porous pot with a stopper fitted with a reflux condenser. This was necessary as the products were of a volatile nature. A sheet lead cathode was used measuring 75 sq. cm. on one side, and a current of 2 amperes for eight hours. The reaction mixture was diluted with water, extracted with ether, the solution dried and fractionated. Seventy per cent. of the product boiled below 120°, 20 per cent. boiled at 190—230°, and a small residue was left in the distilling flask. The total yield of reduced substances weighed 22 grams. The remainder was lost along with the evolved hydrogen at the cathode. The fraction of low boiling point was composed almost entirely of *n*-butyl alcohol. The fraction boiling at 190—230° was a mixture, and was not studied further.

Mesityl Oxide.

Many attempts have been made to follow the course of reduction of mesityl oxide and isolate definite products from the reaction mixture. The experiments have been conducted chiefly in alkaline media, and the products have probably been similar in all cases. Baeyer (*Annalen*, 1866, **140**, 290) first examined a liquid product, to which he assigned the formula $C_{12}H_{22}O$. Claisen (*Annalen*, 1876, **180**, 7) re-investigated and named the reduced compound deoxymesityl oxide, to which the formula $C_{12}H_{20}O$ was given. The above researches were conducted with a mixture, and no substance of constant boiling point was isolated. A more recent investigation has been carried out by Harries and Hübner (*Annalen*, 1897, **296**, 295), and an attempt made to elucidate the constitution of deoxymesityl oxide. The reaction is assumed to take place in stages represented by the following equations:

$$2\mathrm{CMe_2{:}CH{\cdot}COMe} + 2\mathrm{H} = \mathrm{CH_3{\cdot}CO{\cdot}CH_2{\cdot}CMe_2{\cdot}CMe_2{\cdot}CH_2{\cdot}COMe} =$$



$$\mathrm{CMe_2}\left\langle\begin{array}{l}\mathrm{CH_2{-}CMe}\\ \qquad\quad\ \|\\ \mathrm{CMe_2{\cdot}C{\cdot}COMe}\end{array}\right. + \mathrm{H_2O}.$$

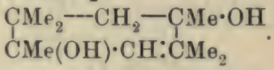
The first step represents the reduction reaction, and the second an inner condensation due to the nature of the medium. These facts are supported by the formation of an oxime, $C_{12}H_{20}{:}NOH,H_2O$, and an oxidation product identical with tetramethylsuccinic acid. The pure compound was not isolated. A different method of reducing mesityl oxide was carried out by Kerp and Müller (*Annalen*, 1894, **290**, 132). The chief product was an alcohol, $C_6H_{14}O$, with a smaller quantity of an oil containing 73·44 per cent. of carbon and 12·16 per cent. of hydrogen, but boiling at approximately the same temperature as deoxymesityl oxide. The compound, $C_{12}H_{20}O$, however, contains 80 per cent. of carbon, whereas the new oil is remarkable for its high percentage of oxygen. The correctness of Harries and Hübner's view was therefore open to some doubt, especially as the oxime mentioned above corresponded with a ketone of the formula $C_{12}H_{20}O,H_2O$ ($C_{12}H_{22}O_2$). Furthermore, these authors apparently assumed that the compound in their hands was identical with Claisen's deoxymesityl oxide without the support of analysis. It seemed possible, therefore, that the mixture in the hands of Harries and Hübner contained at least one substance of the formula $C_{12}H_{22}O_2$, from which the oxime was derived, and that the compound $C_{12}H_{20}O$ was due to decomposition of the compound $C_{12}H_{22}O_2$ or some similar substance. The compound $C_{12}H_{20}O$ was probably formed during repeated fractionation of an original reduction product of the formula $C_{12}H_{22}O_2$. This view was entirely confirmed by the experiments described below. Mesityl oxide was reduced by the electrolytic method, but under conditions as nearly as possible like those described in the work of Harries and Hübner. The product boiled almost entirely at 215—235°, and yielded an oxime identical with that described by Harries and Hübner. It was probably the same mixture as that in the hands of the latter investigators. The formula agreed, however, with $C_{12}H_{22}O_2$. When fractionated, it lost water even under diminished pressure, and was gradually resolved into two products of the formulæ $C_{12}H_{20}O$ and $C_{12}H_{22}O_2$. The latter was a solid, and was obtained quite pure. It readily yielded the oxime already mentioned above. It was saturated, and on oxidation gave an acid identical with tetramethylsuccinic acid. It was stable towards heat, and could be fractionated unchanged, even at atmospheric pressure. It probably had the constitution $COMe\cdot CH_2\cdot CMe_2\cdot CMe_2\cdot CH_2\cdot COMe$. The original reduction product, on the other hand, was highly unsaturated, as was also the compound $C_{12}H_{20}O$, and readily lost water when heated. These facts can be supported best by assuming that at least two of the reactions indicated in the following equations take place:

(1) $2CMe_2{:}CH\cdot COMe + 2H = COMe\cdot CH_2\cdot CMe_2\cdot CMe_2\cdot CH_2\cdot COMe.$

(2) $2H + 2CMe_2{:}CH\cdot COMe = CMe_2{:}CH\cdot CMe(OH)\cdot CMe(OH)\cdot CH{:}CMe_2.$

(3) $2H + 2CMe_2{:}CH\cdot COMe = COMe\cdot CH_2\cdot CMe_2\cdot CMe(OH)\cdot CH{:}CMe_2.$

(4) $2H + COMe\cdot CH_2\cdot CMe_2\cdot CMe(OH)\cdot CH{:}CMe_2 =$



$$\begin{array}{l}CMe_2\text{---}CH_2\text{---}CMe\cdot OH\\ CMe(OH)\cdot CH{:}CMe_2\end{array}.$$

Reduction was carried out in the apparatus already described (*loc. cit.*). Several preliminary experiments were conducted with lead cathodes in order to determine the best working conditions. Both acid and alkaline electrolytes were tried, and were found to exercise a considerable influence on the products of the reaction. Sulphuric acid electrolytes, however, had to be abandoned as the lead of the cathode passed into solution during reduction. The product was a heavy, red oil containing a considerable percentage of lead, but mixed with the better known deoxymesityl oxide. The red oil was easily hydrolysed when boiled with water, leaving a residue of lead hydroxide. A similar reaction took place with many other aliphatic and alicyclic compounds, but the product was in no case investigated further than described above. This curious behaviour of lead cathodes was noticed only in acid solutions, and never in alkaline ones. No similar reaction was detected with copper. The concluding experiments were therefore conducted in alkaline media. The mixture in the cathode cell contained 25 grams of mesityl oxide, 50 c.c. of water, 160 c.c. of alcohol, and 13 grams of potassium hydroxide. A current of 6 amperes was used for five hours. The electrodes had an area of 75 sq. cm. on one side. The temperature rose somewhat as reduction proceeded, and was usually 10° higher than the surrounding atmosphere at the end of the experiment. The product was diluted with water, and the oil extracted with ether. The ethereal extract was dried, and, after the removal of the ether, fractionated under 20 mm. pressure. The following fractions were obtained: (I) b. p. below 93°, 5 grams; (II) b. p. 93—110°, 2·5 grams; (III) b. p. 110—130°, 10 grams. There was also a small residue of higher boiling point. The quantities of these fractions varied somewhat in different experiments, but in every case there was a loss of material amounting to about 20 per cent. of the mesityl oxide used. This loss was finally traced, and was found to be due to the formation of highly volatile products which disappeared during manipulation. An easy method of preparing these fractions of low boiling point was discovered later, and will be dealt with elsewhere.

Fraction I was composed chiefly of unchanged mesityl oxide and a saturated ketone identical with methyl *iso*butyl ketone. The quantity of the latter substance was never very considerable. It yielded a semicarbazone melting at 134°.

Fractions II and III were mixed and boiled at 210—230°/760 mm., with partial decomposition:

0·1278 gave 0·3437 CO_2 and 0·1307 H_2O. C=73·34; H=11·19.
$C_{12}H_{22}O_2$ requires C=72·72; H=11·11 per cent.
$C_{12}H_{20}O$ „ C=80·00; H=11·1 „ „

This mixture therefore contained chiefly compounds of the formula $C_{12}H_{22}O_2$. Water was easily eliminated on distillation, either under diminished or the ordinary pressure. Decomposition was not complete, however, even after boiling for many hours. An attempt was made to isolate pure constituents from the above mixture by fractionation under diminished pressure. This operation was carried out thirty times, and two main fractions were obtained boiling at 107—108°/20 mm. and 122—123°/20 mm. respectively. Neither fraction was quite pure, but they had the approximate formulæ $C_{12}H_{20}O$ and $C_{12}H_{22}O_2$ respectively.

The fraction boiling at 122—123°/20 mm. deposited, after some time, well defined crystals readily soluble in the usual organic solvents. These melted sharply at 53—55°, and were quite pure:

0·1025 gave 0·2730 CO_2 and 0·1060 H_2O. C=72·63; H=11·49.
$C_{12}H_{22}O_2$ requires C=72·72; H=11·11 per cent.

These crystals were quite stable towards heat, and could be distilled without decomposition. They readily yielded an oxime (m. p. 156—157°) identical with that prepared by Harries and Hübner from deoxymesityl oxide. This oxime was converted into the hydrochloride melting and decomposing at 120—125°, which is in agreement with the records of previous investigators.

A small quantity of the original ketone was oxidised by means of chromium trioxide in the manner described by Harries and Hübner. An acid was obtained melting at 190° with effervescence due to the liberation of carbon dioxide. This substance appeared to be identical with tetramethylsuccinic acid. It was formed probably by decomposition according to the following scheme:

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CMe_2{\cdot}CMe_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3 \longrightarrow CO_2H{\cdot}CMe_2{\cdot}CMe_2{\cdot}CO_2H.$$

The formula of the substance $C_{12}H_{22}O_2$ is therefore well established. The original crystals decolorised bromine only very slowly with the liberation of hydrogen bromide. They formed a monosemicarbazone on long keeping in contact with the necessary reagents in the cold. A white, crystalline product was formed, crystallising from benzene and melting at 185—186°:

0·1026 gave 0·2271 CO_2 and 0·0905 H_2O. C = 60·36; H = 9·80.
$C_{13}H_{25}O_2N_3$ requires C = 60·11; H = 9·88 per cent.

It was notable that only one carbonyl group reacted with either hydroxylamine or semicarbazide even on long contact with these reagents.

Numerous attempts were made to find a solvent suitable for crystallising the compound melting at 53—55°. This, however, failed on account of the ready solubility in all the ordinary organic reagents.

The second fraction referred to above and boiling at 107—108°/20 mm. was fractionated under the atmospheric pressure, and lost a further quantity of water. It boiled at 218—220°/760 mm. (Found, C = 79·86; H = 11·57. $C_{12}H_{20}O$ requires C = 80·00; H = 11·11 per cent.)

This substance, therefore, was deoxymesityl oxide in a fairly pure state. It readily absorbed bromine without the liberation of hydrogen bromide, and was therefore unsaturated. An iodine determination was made in the usual manner, when 0·3 gram of deoxymesityl oxide absorbed 30 c.c. of $N/5$-iodine solution. This corresponds with nearly two molecules of iodine per molecule of the original oil. Deoxymesityl oxide was allowed to remain in contact with an aqueous solution of semicarbazide hydrochloride and sodium acetate for several months, when a solid substance was slowly formed. This was crystallised several times from benzene, and was finally separated into two compounds melting respectively at 137° and 161°, the latter being the less soluble:

0·1014 gave 0·2440 CO_2 and 0·0892 H_2O. C = 65·63; H = 9·87.
$C_{13}H_{23}ON_3$ requires C = 65·82; H = 9·70 per cent.

This substance therefore was the *monosemicarbazone* of deoxymesityl oxide. The compound melting at 137° was difficult to obtain pure, and sufficient was not prepared for a complete analysis. There is probably a third solid substance formed, but this was never isolated in a pure state. Deoxymesityl oxide was readily attacked by oxidising agents, but yielded no well defined products. Tetramethylsuccinic acid was not produced.

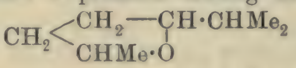
The most probable explanation of the formation of deoxymesityl oxide is that the reaction takes place in two stages. Mesityl oxide is first reduced at the carbonyl group according to equation 2. The product, like many others of a similar nature, readily loses water when heated, and becomes converted into a ketone on similar lines to the pinacone-pinocolin transformation, and represented in an equation as:

$$\mathrm{CMe_2{:}CH{\cdot}CMe(OH){\cdot}CMe(OH){\cdot}CH{:}CMe_2 = H_2O + CMe_2{:}CH{\cdot}CMe_2{\cdot}CO{\cdot}CH{:}CMe_2.}$$

There is, however, the second possibility that the reduction takes place as in equation 3; the product then loses water on distillation, and leads to the introduction of a second double linking, as in the following equation:

$$\mathrm{CH_3{\cdot}CO{\cdot}CH_2{\cdot}CMe_2{\cdot}CMe(OH){\cdot}CH{:}CMe_2 = H_2O + CH_3{\cdot}CO{\cdot}CH_2{\cdot}CMe_2{\cdot}C({:}CH_2){\cdot}CH{:}CMe_2.}$$

Methylheptenone (Natural).

The above product was the naturally occurring oil, to which the formula $\mathrm{CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3}$ has been assigned. The reduction products have been investigated previously by Wallach (*Annalen*, 1893, **275**, 171), who isolated an unsaturated alcohol as the only product. A few preliminary experiments were conducted with the electrolytic method of reduction in order to determine the best working conditions. It was soon found that reduction proceeded very slowly in alkaline solution, even when lead cathodes were used, and the method was abandoned. Sulphuric acid was next tried as electrolyte, when reduction proceeded smoothly and regularly. The product was deep red, and always contained some lead dissolved in it. This lead compound was not isolated in a pure state. The experiment was carried out in the following manner: A mixture of 50 grams of methylheptenone, 150 c.c. of alcohol, and 50 c.c. of 25 per cent. sulphuric acid were reduced, employing a current of 1·5 amperes for twenty-four hours. A lead cathode was used measuring 75 sq. cm. on one side. The whole mixture was then distilled in a current of steam, the distillate extracted with ether and the ethereal solution dried. On removal of the ether a product was obtained amounting to 45 per cent. of the original compound taken. The non-volatile portions left in the distilling flask deposited lead hydroxide. The non-volatile liquid portion weighed 35 per cent. of the methylheptenone reduced. There was always a loss of material of 15 per cent. The volatile portion was fractionated, and yielded two main parts boiling at 110—150° and 150—200° in the proportion of 4:9. The latter was treated with a concentrated solution of sodium hydrogen sulphite to separate the unchanged methylheptenone, and the residual oil refractionated. A product was then isolated boiling at 174—176°/760 mm., and identical with methylheptenol. The fraction of low boiling point was treated in a similar manner, when two main fractions were obtained boiling respectively at 118—125° and 125—135°. The latter on refractionation yielded a product boiling at 127—129° identical with the compound  $CH_2<\begin{array}{l}CH_2-CH\cdot CHMe_2\\ CHMe\cdot O\end{array}$ previously prepared by Wallach by the action of dilute sulphuric acid on methylheptenol. The portion of lower boiling point yielded a fraction boiling at 120—123°, which was evidently a mixture of the above inner ether and a substance rich in carbon, probably an unsaturated hydrocarbon. This hydrocarbon was never isolated in a pure state, but fractions were obtained which readily decolorised bromine, and were readily attacked by cold solutions of potassium permanganate.

The non-volatile portion left over from the steam distillation was also fractionated, but readily decomposed, depositing large quantities of lead compounds. It yielded no product of constant boiling point.

Dimethylmesityloxide.

This substance was prepared by the method already described (Proc., 1907, **23**, 74), and had the probable constitution

$$CH_3\cdot CH_2\cdot C(CH_3)\dot{:}C(CH_3)\cdot CO\cdot CH_3.$$

It is related to methyl ethyl ketone in exactly the same manner as acetone to mesityl oxide. It was reduced and worked up in the same way as in the case of mesityl oxide. The product was fractionated, when the following main portions were obtained under 15 mm. pressure: (I) b. p. 40—95°, 30 per cent.; (II) 145—165°, 45 per cent.; (III) 165—175°, 25 per cent.

Fraction I boiled completely at 160—170°; it had a strong odour of peaches, and contained a considerable amount of unchanged product. It readily yielded a semicarbazone, and thus differed from the parent substance. A small quantity was isolated and crystallised from benzene, when it melted at 125—130°:

0·1015 gave 0·2200 CO_2 and 0·0852 H_2O. C=59·11; H=9·33.

$C_9H_{17}ON_3$ requires C=59·01; H=9·29 per cent.

Reduction therefore had taken place at the double linking to produce a saturated ketone. The quantity present was small, and did not permit of further investigation. The compound analysed was probably a mixture of two isomeric semicarbazones.

Fractions II and III were treated together. They were redistilled and separated into two main portions boiling respectively at 135—138°/15 mm. and 172—173°/15 mm., but at the same time a considerable amount of water was eliminated. The fraction of lower boiling point was redistilled under the atmospheric pressure, when it boiled chiefly at 250—260°, but still lost water. A fraction was finally obtained boiling at 254—256°, which gave the following results on analysis:

0·1367 gave 0·4090 CO_2 and 0·1490 H_2O. C = 81·67; H = 12·11.

$C_{16}H_{28}O$ requires C = 81·35; H = 11·86 per cent.

The fraction boiling at 172—173°/15 mm. was by far the larger, and on analysis gave the following results:

0·1550 gave 0·4300 CO_2 and 0·1673 H_2O. C = 75·61; H = 11·98.

$C_{16}H_{32}O_2$ requires C = 75·59; H = 11·90 per cent.

The reduction of dimethylmesityl oxide had proceeded, therefore, in practically the same manner as mesityl oxide itself. The main course of the reaction took place according to the equation:

$$2C_8H_{14}O + 2H = C_{16}H_{30}O_2.$$

The product $C_{16}H_{30}O_2$ was a mixture of at least two compounds, one stable and the other unstable at the boiling point. The latter lost water on distillation, and yielded a substance of lower boiling point, $C_{16}H_{28}O$, which was then stable at its boiling point.

Citronellaldehyde.

This substance was extremely difficult to reduce, even when lead cathodes were employed. Electrodes of the highest known supertension were employed, namely, amalgamated lead or zinc, but even then reduction took place so slowly that the investigation was abandoned.

Citral.

The reduction products of citral have been recently investigated by two authors. Verley (*Bull. Soc. chim.*, 1899, [iii], **21**, 409) obtained chiefly a complex substance of high boiling point (203—205°/15 mm.), to which he assigned the pinacone formula, $C_9H_{15}\cdot CH(OH)\cdot CH(OH)\cdot C_9H_{15}$. Skita (*Ber.*, 1909, **42**, 1635) obtained a crystalline substance in a pure state. It was expected that one of these compounds would be produced by the electrolytic method of reduction. The experiments were conducted with citral obtained from lemon-grass oil by fractionation, and was probably a mixture of two closely allied aldehydes. Reduction was first carried out in alkaline solution, and a viscid, oily substance was obtained as sole product, but identical with that produced in the concluding experiments. The reaction was finally carried out in the presence of sulphuric acid, when a variety of products was isolated.

The cathode solution contained 25 grams of citral, 150 c.c. of alcohol, 50 c.c. of water, and 20 grams of sulphuric acid. A lead cathode of 75 sq. cm. superficial area on one side was used, and a current of 2·5 amperes for twelve hours. The current, however, fell off considerably as the experiment proceeded, and was usually 0·5 ampere at the finish. Twenty ampere-hours were supplied for each experiment. The product was usually red, and contained considerable quantities of dissolved lead. It was distilled in a current of steam, and the volatile portion extracted with ether and finally fractionated. A small quantity of water eliminated during distillation, and a mixture of hydrocarbons was obtained, boiling at 165—185°. This could not be divided into pure constituents, but corresponded in formula with anhydrogeraniol. The remainder boiled at 210—235°, and was a mixture of at least two alcohols. The main fraction boiled at 217—220°, and on analysis yielded the following results:

0·1024 gave 0·2940 CO_2 and 0·1082 H_2O. C = 78·10; H = 11·64.

$C_{10}H_{18}O$ requires C = 77·92; H = 11·69 per cent.

This substance therefore was isomeric with geraniol. It was fairly stable towards heat, but decomposed slowly at its boiling point with loss of water and the formation of the above hydrocarbons. It readily lost water when treated with most reagents even in the cold, with the formation of the above mixed hydrocarbons. Sodium hydrogen sulphite solution, phthalic anhydride, phosphorus penta- and tri-chlorides all split off water. Diphenylcarbamyl chloride and pyridine on the water-bath caused the same decomposition, but at the same time a small quantity of a solid melting at 82° was formed, which indicated the presence of geraniol. It seemed probable, therefore, that two alcohols were present, one of which was the known geraniol, but the main portion was an unstable isomeric alcohol boiling at about 220°. This was never obtained quite pure on account of its unstable nature.

The non-volatile portion left in the steam distillation flask was extracted with ether and fractionated. It boiled at 210—280°/25 mm., the main portion being obtained at 216—220°/25 mm. The latter was isolated, and on analysis gave the following results:

0·1048 gave 0·3138 CO_2 and 0·1054 H_2O. C = 81·68; H = 11·11.
$C_{20}H_{34}O_2$ requires C = 78·43; H = 11·11 per cent.
$C_{20}H_{32}O$ „ C = 83·33; H = 11·11 „ „

Reduction, therefore, had probably proceeded according to the equation:

$$2C_{10}H_{16}O + 2H = C_{20}H_{34}O_2$$

in a manner similar to that occurring in the case of mesityl oxide. The compound $C_{20}H_{34}O_2$ then lost water when fractionated, and became partly converted into the compound $C_{20}H_{32}O$. The compound $C_{20}H_{34}O_2$ was probably the same as that obtained by Verley, and of the nature of a pinacone. It was highly unsaturated and without aldehydic properties. It was unstable towards heat, and lost water when distilled. The compound described by Skita was not present.

Menthone.

This substance has been previously investigated by Beckmann (*J. pr. Chem.*, 1897, [ii], **55**, 18 and 30), who obtained a mixture of menthol and menthopinacone on reduction with sodium. It was expected that the same products would be obtained by the electrolytic method which was tried, using an alkaline electrolyte. Reduction, however, proceeded very slowly, even when lead cathodes were used. The acid medium was next tried, and satisfactory results were obtained. Reduction proceeded readily, and was soon complete. Twenty-five grams of menthone, 150 c.c. of alcohol, 50 c.c. of water, and 10 grams of sulphuric acid were treated. A lead cathode was used, measuring 75 sq. cm. on one side. A current of 2 amperes was passed through this mixture for twelve hours (overnight). The product was distilled in a current of steam, and the volatile portion extracted with ether. The distillate was composed chiefly of menthol, and amounted to 82 per cent. of the original menthone. The viscid, oily residue in the steam distillation flask was allowed to remain for several days, when it deposited large, colourless crystals. These were separated by filtration, and amounted to 10 per cent. of the total product. They crystallised from alcohol in large cubes closely resembling sodium chloride in appearance. These crystals could easily be obtained quite perfect in shape, and with sides 5 cm. long. They melted at 172—173°:

0·1016 gave 0·2873 CO_2 and 0·1140 H_2O. C = 77·12; H = 12·46.
$C_{20}H_{38}O_2$ requires C = 77·42; H = 12·26 per cent.

A second crop of crystals melting at 148—150° was obtained from the mother liquors:

0·1004 gave 0·2848 CO_2 and 0·1120 H_2O. C = 77·36; H = 12·39.

These two substances therefore were isomeric menthopinacones, but neither was identical with the one described by Beckmann (*loc. cit.*), which melted at 94°. The quantity of material in hand was small, and further experiments were not undertaken as the results agreed with past experience.

Carvone.

Carvone has been carefully investigated by many authors, and a variety of well defined reduction products has been isolated. Reaction takes place generally at the double link in the ring, and two main products are obtained, namely, dihydrocarvone and α-dicarvelone. The double link in the side-chain does not appear to be readily attacked, and usually persists in the reduction product. The product of electrolytic reduction was similar to those already recorded, and differed chiefly in the formation of a much larger percentage yield of dicarvelone.

The carvone used in the following experiments was obtained from the oil of caraway. It was purified by conversion into the hydrosulphide. The latter was crystallised in the usual manner, and melted at 212°, considerably higher than previously recorded. The liberated carvone boiled at 225°, and had α_D^{18} 61°35″. It was therefore quite pure, a fact confirmed by analysis. The pure carvone was easily reduced in both acid and alkaline solutions, and the concluding experiments were conducted in the latter medium to avoid the formation of products containing lead.

The cathode solution contained 50 grams of carvone, 100 c.c. of water, 200 c.c. of alcohol, and 18 grams of potassium hydroxide. Lead cathodes were employed, measuring 75 sq. cm. on one side. The current was 3 amperes at the beginning of each experiment, but fell to 0·5 ampere at the finish. Each experiment was allowed to proceed for twelve hours (overnight), when a semi-solid product was formed. The crystals were removed by filtration, and the oily filtrate allowed to remain for several weeks to deposit more of the solid. The total yield of the latter amounted to 50 per cent. of the carvone taken. The oily residue was extracted with ether, and fractionated under diminished pressure. Practically the whole product distilled at 280—290°/70 mm. It was a viscid, colourless oil, and appeared identical with that previously recorded (Harries, *Ber.*, 1899, **32**, 1316). It was refractionated, and boiled at 260—262°/40 mm. Similar experiments conducted with sulphuric acid as electrolyte and a much larger percentage of the oil was obtained (90—95 per cent.) at the expense of the crystals.

The solid compound obtained above was crystallised from alcohol and melted at 150—151°, which is slightly higher than that previously recorded. It was obtained in large, flat prisms, which could easily be grown to a considerable size. It appeared to be identical with α-carvelone. The mother liquor deposited a further crop of crystals on keeping, which proved to be a mixture of two compounds, the one described above and a second compound forming diamond-shaped crystals. These were separated by allowing an alcoholic solution to evaporate slowly, when large crystals were produced and separated mechanically. The new substance melted at 149—150°, which is practically the same as for α-carvelone. The two compounds were analysed, and yielded the following results:

(1) M. p. 150—151°:

0·1000 gave 0·2910 CO_2 and 0·0900 H_2O. C=79·36; H=10·00.

(2) M. p. 149—150°:

0·1002 gave 0·2914 CO_2 and 0·0904 H_2O. C=79·31; H=10·02.

$C_{20}H_{30}O_2$ requires C=79·47; H=9·93 per cent.

These two substances were therefore isomeric. α-Carvelone is slightly lævorotatory, and yields an oxime melting at 228°, which is somewhat higher than previously recorded. The new compound is slightly dextrorotatory, and yields an oxime melting at 171—173°. The latter is very soluble in alcohol or benzene, but insoluble in light petroleum. It was purified by recrystallisation from a mixture of alcohol and water, but did not melt sharply:

0·1006 gave 0·2654 CO_2 and 0·0940 H_2O. C=71·94; H=10·38.

$C_{10}H_{16}ON$ requires C=72·29; H=9·64 per cent.

It was therefore the dioxime of the new carvelone, but in a slightly impure state. The two carvelones above mentioned are not stereoisomerides. A mixture of equal quantities of each forms an inactive product melting at 121°, which happens to be the same as racemic α-carvelone. The oxime, however, of the mixed carvelones has not a sharp melting point, and is not identical with the oxime of racemic carvelone (m. p. 287°). These two compounds therefore appear to be structurally different.

The oily product referred to above deposited a further crop of crystals on long keeping, and could not be obtained in a pure state.

Pulegone.

The reduction products of pulegone have been studied by many investigators. Tiemann and Schmidt (*Ber.*, 1896, **29**, 914) isolated pulegol, and Beckmann and Pliessner (*Annalen*, 1891, **262**, 30) obtained menthol as a final product. The reaction in both cases took place most readily at the ketone group. Harries and Roeder (*Ber.*, 1899, **32**, 3367) obtained a bimolecular reduction product, 10 per cent. of which was crystalline and melted at 118—119°. The latter substances probably had the pinacone structure in consideration of the easy reducible nature of the carbonyl radicle. Past experience has shown, however, that reduction frequently takes place at both the double linking and the carbonyl group simultaneously. It is notable that menthone was not produced in any considerable quantity, although it is fairly stable towards alkaline reducing agents.

The first experiments tried by the electrolytic method were conducted in alkaline medium. Thirty grams of pulegone, 150 c.c. of alcohol, 100 c.c. of water, and 15 grams of potassium hydroxide were treated overnight (twelve hours), a current of 2 amperes being used. The cathode measured 75 sq. cm. on one side, and was composed of sheet lead. The product was distilled in a current of steam. The volatile portion weighed 10 grams, and was pure menthone. The residue in the distilling flask was extracted with ether, dried, and allowed to remain exposed to the air for several days. Crystals were deposited, which were collected and recrystallised from alcohol. These melted sharply at 119°, and were identical with those described by Harries and Roeder (*loc. cit.*). They were entirely devoid of ketonic properties, and had the formula $C_{20}H_{34}O_2$. They were probably pulego-pinacone. A second substance was also obtained, melting at 148°. This appeared to be the menthopinacone described above, but the quantity was too small to investigate further. The residual oil remained liquid, even on long keeping. It was of an unreactive character, and was not investigated further. It constituted the bulk of the non-volatile portion.

A second reduction experiment was conducted, in which sulphuric acid replaced potassium hydroxide as electrolyte. The product was treated exactly as before. The volatile portion weighed 14 grams, and was a mixture of menthol and menthone. The latter was removed as the semicarbazone, and the former obtained as a liquid boiling at 214—216°. The relative quantity of each varied somewhat, but the main portion was menthol. The non-volatile portion was similar in character to that already described. It would appear, therefore, that pulegone follows the usual rule on reduction. The reaction proceeds at both the double linking and the carbonyl group simultaneously.

Cinnamaldehyde.

This substance readily resinifies on reduction in both acid and alkaline medium. The reaction was therefore tried in a nearly neutral electrolyte (Trans., 1911, **99**, 1114). Five grams of cinnamaldehyde, 25 c.c. of alcohol, 20 c.c. of ethyl acetate, 20 c.c. of water, and 4 grams of potassium acetate were electrolysed with a current of 1 ampere for three hours. A lead cathode was employed, and a current density of 0·05 amperes per sq. cm. The product was diluted with water, extracted with ether, dried, and fractionated under diminished pressure. Two fractions were obtained, namely, (I) b. p. 100—200°/25 mm., and (II) b. p. 200—300°/25 mm. There was also a portion of higher boiling point. Fraction I was treated with a solution of sodium hydrogen sulphite to remove the unchanged aldehyde. The residue boiled at 235°/760 mm., and was β-phenylpropyl alcohol, the yield being 55 per cent. Fraction II could not be identified. The following results were obtained in three parallel experiments:

Cathode material	Copper	Lead	Lead
Temperature	20—30°	20—30°	40—50°
β-Phenylpropyl alcohol...	20 per cent.	55 per cent.	25 per cent.
High boiling fraction	60 ,,	20 ,,	40 ,,

These results agree substantially with those previously recorded (*loc. cit.*).

Styryl Methyl Ketone.

Harries and Hübner have already studied the reduction products of this substance (*Annalen*, 1897, **296**, 295). These authors found it necessary to conduct the reaction in a neutral medium to avoid the excessive formation of resins. The products were benzylacetone, and the bimolecular compound dibenzyldiacetone. The electrolytic method yielded similar results. A resinous, semicrystalline product was formed in both acid and alkaline media, and the concluding experiments were conducted in the almost neutral electrolyte (*loc. cit.*). The cathode compartment contained 5 grams of styryl methyl ketone, 15 c.c. of ethyl acetate, 30 c.c. of alcohol, 30 c.c. of water, and 4 grams of potassium acetate. A current of 1 ampere was used, and reduction was complete in four hours. The product was extracted with ether, dried, and distilled. Two fractions were obtained, namely, (I) b. p. 140—160°/30 mm., and (II) b. p. 240—260°/30 mm. There was also a portion of higher boiling point. Fraction I was benzylacetone, and boiled at 235°/760 mm. Fraction II solidified on cooling, and melted at 161°. This was the dibenzyldiacetone previously recorded (*loc. cit.*). The following results were obtained in two experiments:

Cathode material	Copper	Lead
Temperature	20—30°	20—30°
Benzylacetone	55 per cent.	75 per cent.
Dibenzyldiacetone	35 ,,	20 ,,

p-*Methoxystyryl Methyl Ketone.*

The above substance was reduced by Harries and Hübner (*loc. cit.*) in the manner already described. The products were anisylacetone and dianisyldiacetone. The electrolytic method yielded similar results. Five grams of *p*-methoxystyryl methyl ketone, 20 c.c. of ethyl acetate, 35 c.c. of alcohol, 20 c.c. of water, and 4 grams of potassium acetate were treated exactly as in the previous experiment. The products were an oil boiling at 277°/760 mm., and a solid melting at 151—152°. These were respectively anisylacetone and dianisyldiacetone. There was also a product of higher boiling point. The results of comparative experiments are given below:

Cathode material	Copper	Lead
Temperature	20—30°	20—30°
Anisylacetone	50 per cent.	75 per cent.
Dianisyldiacetone	20 ,,	12 ,,

Conclusions.

The electrolytic method of reduction offers many advantages. It is completely under control, and requires very little attention. The reaction mixture is clean and easy to manipulate. It possesses two disadvantages, which greatly restrict its general application. No organic solvent has yet been used that does not readily mix with water. The choice, therefore, is somewhat restricted. The temperature of reduction may not exceed the boiling point of water or of second solvent used. The reduction of very stable substances at higher temperatures, therefore, may not be attempted.

Reduction proceeds in a manner similar to that effected by sodium or sodium amalgam. This resemblance is greatest when an alkaline medium and a cathode composed of lead are employed. The reaction is somewhat different when an acid electrolyte is used. Reduction takes place much more vigorously, and the material of the cathode frequently enters into combination with the intermediate or final products. The latter phenomenon greatly detracts from the utility of lead as the cathode material. Fortunately the reaction is not the same for all metals, and is entirely absent from copper, tin, amalgamated lead or zinc, and many others. Sheet tin or amalgamated lead are therefore suggested as substitutes for lead, and both come very high in the supertension series.

Unsaturated aldehydes and ketones, containing two reducible groups in a conjugated position, are easier to reduce than compounds with only one reducible group or with two groups widely separated. These facts confirm the now generally accepted view that pairs of double linkings in one molecule mutually augment the properties of the other when brought together into an adjacent position. Each double linking preserves its individuality, however, and reduction may take place at either or both simultaneously. Reduction probably takes place in stages, and commences at the most reactive atom. The starting point of the attack depends on circumstances. The doubly linked carbon pair adds on hydrogen towards the centre of the system. The reverse holds for the carbonyl group, as the oxygen is the most reactive. The reaction thus takes place in one of two directions as represented below:

$$R_2C{:}CH{\cdot}CH{:}O + H \longrightarrow \left[\begin{array}{l} \rightarrow R_2C{\cdot}CH_2{\cdot}CH{:}O \\ \rightarrow R_2C{:}CH{\cdot}CH{\cdot}O\dot{H} \end{array}\right.$$

The two intermediate products act differently according to the conditions. A second atom of hydrogen may be added, two molecular parts may join together, or the metal of the cathode may be attached. The second atom of hydrogen is most readily added in the presence of metallic catalysts. The polymerisation takes place most readily in alkaline solution, and when reduction is undertaken at medium potential. Metallic compounds are formed only in acid solution and with metals like lead, which are slowly attacked by the electrolyte alone, but never with the nobler metals such as copper and mercury.

In conclusion, I wish to express my thanks to the Government Grant Committee for partly defraying the expense of this research

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CVII.—*Aromatic Antimony Compounds. Part III. Some Primary Aryl Derivatives.*

By PERCY MAY.

MANY of the most important primary aryl arsenic compounds are readily obtained by heating arsenic acid with aromatic compounds, such as primary amines and phenols. The corresponding antimony compounds cannot be obtained in this way, and an attempt was therefore made to obtain some of them by other methods. The results obtained up to the present, although incomplete, are now published owing to a lengthy unavoidable interruption of this work, and to the publication of similar researches by Morgan and Micklethwait (Trans., 1911, **99**, 2288).

Phenylstibinic acid, $C_6H_5SbO(OH)_2$, was prepared according to Hasenbäumer's method (*Ber.*, 1898, **31**, 2910; compare Morgan and Micklethwait, *loc. cit.*; Michaelis and Günther, *Ber.*, 1911, **44**, 2316), but owing to a side reaction it was found necessary to devise a method for the further purification of the product. Phenylstibinic acid on nitration gives rise to a mononitro-derivative, from which, by reduction, a small yield of antimonylaniline,

$$NH_2\cdot C_6H_4\cdot SbO,$$

was obtained:

$$C_6H_5\cdot SbO(OH_2) \longrightarrow NO_2\cdot C_6H_4\cdot SbO(OH)_2 \longrightarrow$$

$$\begin{tikzcd} & NH_3Cl\cdot C_6H_4\cdot SbOCl_2 \\ NH_2\cdot C_6H_4\cdot SbO \arrow[ur] \arrow[dr] & \\ & NH_2\cdot C_6H_4\cdot SbO(OH)\cdot ONa \end{tikzcd} .$$

This compound by gentle oxidation yields aminophenylstibinic acid, which was isolated in the form of its hydrochloride, the yield being very small on account of experimental difficulties. This hydrochloride does not appear to be that of the free acid, $HCl,NH_2\cdot C_6H_4\cdot SbO(OH)_2$, but that of the acid chloride,

$$HCl,H_2N\cdot C_6H_4\cdot SbOCl_2.$$

This formation of the acid chloride in aqueous solution is a somewhat remarkable and surprising fact, but the author's work on triphenylstibine derivatives (Trans., 1910, **97**, 1958) shows that the hydroxyl groups in compounds of the type $R_3Sb(OH)_2$ are readily displaced by chlorine, and so this result in the case of aminophenylstibinic acid, $NH_2C_6H_4\cdot SbO(OH)_2$, is not so extraordinary as it first appeared to be. A small quantity of the sodium salt, probably $NH_2\cdot C_6H_4\cdot SbO(OH)\cdot ONa$, was also isolated, but not in a pure condition.

An attempt was made to reduce nitrophenylstibinic acid directly to aminophenylstibinic acid (that is, to reduce the nitro-group to the amino-group without reducing quinquevalent antimony to the tervalent condition) by means of sodium amalgam and methyl alcohol, and also by using ammonium sulphide. In neither case was the attempt successful.

Attempts were also made to obtain the antimony analogue of azobenzene and arsenobenzene, $C_6H_5\cdot Sb\colon Sb\cdot C_6H_5$, by the reduction of phenylstibinic acid, and by the action of sodium on a benzene solution of phenylstibine dichloride, $C_6H_5\cdot SbCl_2$, but without success.

EXPERIMENTAL.

Preparation of Phenylstibinic Acid.—Fifty-seven grams of triphenylstibine were heated with 74 grams of antimony trichloride and a small quantity of xylene in five sealed tubes for forty-eight hours at 240°. The black product was filtered from solid matter, extracted several times with hydrochloric acid, and dried over calcium chloride.* It was then distilled under diminished pressure in a current of carbon dioxide, and the chief fraction collected at 150—190°/25—30 mm. This fraction consisted of a viscid oil, which did not crystallise at all readily, but in some cases deposited a few crystals, and still appeared to contain small quantities of antimony trichloride which could not be extracted from the xylene solution with hydrochloric acid. Some more antimony trichloride had been contained in the first runnings, and the fraction of higher boiling point contained diphenylstibine chloride and unchanged triphenylstibine.

The main fraction, consisting of phenylstibine dichloride, $C_6H_5\cdot SbCl_2$, with smaller quantities of diphenylstibine chloride, $(C_6H_5)_2SbCl$, and antimony trichloride, was dissolved in ice-cold ether and treated with chlorine. After evaporation of the ether, an oily residue consisting of phenylstibine tetrachloride, $C_6H_5\cdot SbCl_4$, contaminated with diphenylstibine trichloride, $(C_6H_5)_2SbCl_3$, and traces of antimony pentachloride, was obtained. This was hydrolysed with aqueous ammonia, and the liquid filtered. The residue consisted of triphenylstibine dichloride, diphenylstibinic acid, $(C_6H_5)_2SbO_2H$, and antimonic acid, and the filtrate contained the ammonium salt of phenylstibinic acid. The latter was acidified with dilute sulphuric acid, whereby the acid was precipitated. Twenty-six grams of the crude acid were obtained. In order further to purify the substance, it was dissolved in aqueous sodium carbonate solution, and filtered from a slight insoluble residue consisting probably of antimonic acid and diphenylstibinic acid. The pure acid was then precipitated by acidifying with dilute sulphuric acid. In this way phenylstibinic acid was obtained as a white, microcrystalline powder, which in the moist state possesses a faint characteristic and not unpleasant odour.

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* Great care is necessary in working with these substances. The vapours, when hot, are excessively irritant, and a drop of a dilute xylene solution of the reaction product, allowed to come into contact with the skin, produced a painful sore, the effect lasting for some days.

Nitration of Phenylstibinic Acid.—This was carried out in a similar fashion to that described by Morgan and Micklethwait (Trans., 1911, **99**, 2296), and the product obtained resembled the *m*-nitrophenylstibinic acid described by these investigators. Some of the crude acid containing both the phenylstibinic and diphenylstibinic acids was nitrated in the same manner, and the product found to contain 5·9 per cent. of nitrogen. It was therefore probably a mixture of nitrophenylstibinic and dinitrodiphenylstibinic acids. After dissolving in glacial acetic acid, the first crop of crystals consisted of needles melting at 210—213°, and contained 7·2 per cent. of nitrogen, and therefore was the di-*m*-nitrodiphenylstibinic acid described by Morgan and Micklethwait (*loc. cit.*).

Reduction of m-*Nitrophenylstibinic Acid.*—Five grams of nitrophenylstibinic acid were gently warmed on the water-bath for two hours with 18 grams of tin and an excess of 4*N*-hydrochloric acid, to which a few grams of glacial acetic acid had been added. The solution containing the hydrochloride of the base was filtered, excess of sodium hydroxide added, and the precipitated base washed several times by decantation with sodium hydroxide solution, and finally with water. The precipitate, which in the moist state has an odour somewhat resembling that of dimethylaniline and of α-naphthylamine, was collected and dried, the final product consisting of 2·6 grams of a pale yellow powder. It is soluble in hydrochloric acid, forming solutions which give the diazo-reaction, but give no precipitate with hydrogen sulphide. The substance is therefore an aromatic primary amine, and is free from tin and inorganic antimony.

Found: $N=5{\cdot}9$; Sb(as Sb_2O_4)$=52{\cdot}94$.

C_6H_6ONSb requires $N=6{\cdot}14$; $Sb=52{\cdot}63$ per cent.

m-*Antimonylaniline*, $NH_2{\cdot}C_6H_4{\cdot}SbO$, is a yellow powder, insoluble in water or alkali, soluble in acids, and sparingly so in alcohol. It could not be obtained in well-defined crystals, and it has no definite melting point, but begins to soften and decompose below 200°. The vapour (or fine dust) has an extraordinarily strong irritant action on the nose, throat, and eyes, causing prolonged and violent fits of sneezing.

Oxidation of m-*Antimonylaniline.*—Dilute alkaline hydrogen peroxide was gradually added to 2 grams of antimonylaniline until the latter was almost completely dissolved, and the mixture then warmed on the water-bath until evolution of oxygen ceased. The liquid was filtered, and a small portion of the filtrate acidified with dilute sulphuric acid. No precipitate was produced, but the liquid gave the diazo-reaction, showing that the amino-group had not been destroyed. On acidifying another portion with hydrochloric acid, a crystalline precipitate was produced, and the main bulk of the liquid was therefore acidified with hydrochloric acid and maintained at 70° for two hours. After being set aside for fifteen hours, the precipitate was separated and washed with hydrochloric acid. After drying in a vacuum, 0·34 gram of a silky, crystalline substance was obtained. A small additional quantity of the substance was isolated by evaporation of the mother liquors and extraction of the product with alcohol.

A further quantity (0·14 gram) was prepared by the reduction of another 1·7 grams of *m*-nitrophenylstibinic acid and oxidation of the product by means of sodium peroxide in aqueous suspension.

The substance is soluble in water, forming an acid solution, which can be diazotised. This solution gives a precipitate of silver chloride on treatment with nitric acid and silver nitrate, and is reprecipitated by excess of hydrochloric acid. On heating, it decomposes and blackens, evolving pungent fumes; it does not give the reactions of antimony salts, but does so after fusion with sodium peroxide.

The first preparation gave Cl = 31·8, and the second preparation gave Cl = 32·0. Mean = 31·9.

$HCl,H_2N{\cdot}C_6H_4{\cdot}SbO(Cl)_2$ requires Cl = 31·7 per cent.,

and therefore the substance appears to be probably the *hydrochloride* of *aminophenylstibinyl chloride*, instead of that of the free acid, which requires Cl = 11·9 per cent.

Attempt to Prepare the Sodium Salt of Aminophenylstibinic Acid.

2·26 Grams of nitrophenylstibinic acid were reduced and oxidised as before, but the alkaline filtrate, instead of being acidified with hydrochloric acid, was evaporated to dryness. The product was then extracted with absolute alcohol in a Soxhlet apparatus, and a small quantity of a pale brown, crystalline solid was obtained. This substance chars on heating, and is readily soluble in water. The aqueous solutions have a slightly alkaline reaction, and give a faint diazo-reaction after acidifying with dilute sulphuric acid. Hydrochloric acid produces a slight crystalline precipitate.

The substance is therefore probably the slightly impure sodium salt of aminophenylstibinic acid.

The expenses of this investigation have been defrayed by a grant from the Research Fund Committee of the Chemical Society.

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CVIII.—*Aromatic Antimony Compounds. Part IV. Compounds of Antimony Trichloride with Diazonium Chlorides.*

By Percy May.

Additive compounds of diazonium chlorides with salts of heavy metals have been described by Hantzsch (*Ber.*, 1895, **28**, 1734), some, such as the mercuric salts, $C_6H_5\cdot N_2Cl,HgCl_2$, being regarded as double salts of the true diazonium chlorides; but others, such as the cuprous salts, $C_6H_5\cdot N_2Cl,Cu_2Cl_2$, being regarded as *syn*-diazochlorides. As antimony trichloride seems, in an exceptional degree, to possess the power of forming additive compounds, it became a matter of interest to see whether it would combine with diazonium chlorides, and, if so, to ascertain to which type these compounds would belong.

Antimony trichloride forms crystalline additive compounds with diazonium chlorides, which are colourless, or nearly so, except in those cases where the parent diazonium chloride is coloured, and are practically insoluble in water and the usual organic solvents; indeed, antimony chloride can be completely precipitated from acid solutions by addition of an excess of diazonium chloride. The stability of these compounds is far greater than that of the parent diazonium chlorides, and they can be handled in the dry state without fear of explosion; but they decompose more or less vigorously when heated. On boiling with water they are decomposed with evolution of nitrogen, although more slowly than in the case of the parent compound; the nature of the product depends to some extent on the character of the particular diazonium chloride, although it generally resembles that of the parent substance.

The foregoing properties, with the exception of the insolubility in water which appears to be a special characteristic of these antimony compounds, are undoubtedly those of a diazonium chloride rather than those of a *syn*-diazo-chloride.

In the case of the additive compounds derived from α- and β-naphthyldiazonium chlorides, small quantities of the corresponding chloronaphthalenes appear to be formed on boiling with water, and it is significant that these compounds are of a slightly more marked brown colour than are those derived from the simple aromatic diazonium chlorides. This would seem to indicate that in these compounds there exists a solid solution of the *syn*-diazo-chloride in the diazonium chloride.

The compounds here described were in every case obtained by diazotising the base in presence of hydrochloric acid, an excess of which was then added, followed by the addition of a solution of antimony trichloride in hydrochloric acid in insufficient quantity to combine with all the diazonium chloride. The resultant crystalline precipitate was then separated and washed, first with hydrochloric acid and then with water, and dried under diminished pressure.

In general, the compounds formed contain one molecule of antimony trichloride to one diazonium chloride group, but in the case of benzidine a well crystallised intermediate compound was also obtained containing only one molecule of antimony chloride to the two diazonium groups.

The following compounds of this type have been prepared:

The *compound* with benzenediazonium chloride forms white leaflets. When heated with water to 80°, it yields a mixture of phenol and diphenyl, the formation of the latter being due to the slight reducing action of the antimony trichloride:

$$SbCl_3 + 2C_6H_5{\cdot}N_2Cl = SbCl_5 + 2N_2 + C_6H_5{\cdot}C_6H_5.$$

If the decomposition is carried out at a higher temperature by passing steam into the liquid, the products are the same, but the amount of phenol formed is increased.

Found: N = 7·2; Cl = 38·1.

$C_6H_5N_2Cl,SbCl_3$ requires N = 7·6; Cl = 38·7 per cent.

The *compound* with *o*-toluenediazonium chloride resembles the preceding derivative in its properties and reactions.

Found: N = 7·9.

$C_7H_7N_2Cl,SbCl_3$ requires N = 7·4 per cent.

The *compound* from *p*-toluenediazonium chloride is similar to that from the *o*-compound.

Found: N = 7·8.

$C_7H_7N_2Cl,SbCl_3$ requires N = 7·4 per cent.

The *compound* from *p*-chlorobenzenediazonium chloride forms beautiful, white crystals, which decompose only very slowly on boiling with water, forming very small quantities of *p*-chlorophenol with more 4:4′-dichlorodiphenyl.

Found: N=6·9.

$C_6H_4N_2Cl_2,SbCl_3$ requires N=7·0 per cent.

The *compound* from *m*-nitrobenzenediazonium chloride crystallises in colourless leaflets which slowly decompose on boiling with water, yielding a little nitrophenol.

Found: N=8·7; Cl=44·5.

$C_6H_4O_2N_3Cl,SbCl_3,2HCl$ requires N=8·7; Cl=44·0 per cent.

The *compound* from α-naphthalenediazonium chloride forms a brown, amorphous precipitate, which decomposes on boiling with water, yielding small quantities of α-naphthol and α-chloronaphthalene, together with azo-compounds and a considerable amount of tarry matter.

Found: N=5·9; Cl=37·8.

$C_{10}H_7N_2Cl,SbCl_3,HCl$ requires N=6·1; Cl=38·8 per cent.

The *compound* from β-naphthalenediazonium chloride resembles the α-compound in its properties and in its decomposition products.

Found: N=6·4; Cl=39·7.

$C_{10}H_7N_2Cl,SbCl_3,HCl$ requires N=6·1; Cl=38·8 per cent.

The *compound* from diphenylbisdiazonium chloride,

$C_{12}H_8N_4Cl_2,SbCl_3,HCl$,

is obtained by tetrazotising benzidine in hydrochloric acid solution, and then adding approximately one molecular portion of antimony trichloride solution. It crystallises in splendid needles, which are at first of a coppery tinge, but become colourless on washing with water.

Found: N=10·2; Cl=36·7.

$C_{12}H_8N_4Cl_2,SbCl_3,HCl$ requires N=10·3; Cl=35·7 per cent.

This compound decomposes on heating more violently than the other additive compounds here described. When warmed with water to 80° it gives a good yield of 4:4′-diphenol, this being the only product isolated.

A second *compound* from diphenylbisdiazonium chloride,

$C_{12}H_8N_4Cl_2,2SbCl_3,2HCl$,

is prepared from benzidine in the usual manner. It forms a white, crystalline precipitate, which yields 4:4′-diphenol when boiled with water:

Found: N=6·9; Cl=44·3.

$C_{12}H_8N_4Cl_2,2SbCl_3,2HCl$ requires N=7·0; Cl=44·1 per cent.

The *compound* from 2-nitrodiphenylbisdiazonium chloride is a yellow, crystalline precipitate. When heated with water it yields impure 2-nitro-4:4-diphenol, which, like that prepared from the solutions of the parent bisdiazonium chloride, is very difficult to purify. The product dissolves in alkali with a blood-red colour, and has all the properties of the nitrophenol prepared directly.

Found: N = 8·6; Cl = 42·6.

$C_{12}H_7O_2N_5Cl_2,2SbCl_3,2HCl$ requires N = 8·3; Cl = 41·8 per cent.

The *compound* from 3:3′-dimethoxydiphenylbisdiazonium chloride, prepared from *o*-dianisidine, is obtained as a brown precipitate. On warming with water, no phenol was obtained, but only the insoluble "quinonoid" compound obtained by Cain in this way from the parent bisdiazonium compound (Trans., 1903, **83**, 688).

Found: N = 6·4; Cl = 42·1.

$C_{14}H_{12}O_2N_4Cl_2,2SbCl_3,2HCl$ requires N = 6·5; Cl = 41·1 per cent.

It will be seen from the foregoing account that in the diphenyl derivatives the behaviour of the antimony trichloride additive compounds, when heated with water, does not differ from that of the parent bisdiazonium chlorides. Both in the case of the naphthalene and diphenyl derivatives, one molecule of hydrogen chloride appears to unite with the antimony trichloride, but this is not the case in the simple benzene derivatives, except in the case of *m*-nitrobenzenediazonium chloride, where the antimony trichloride is accompanied by two molecules of hydrogen chloride.

The diazonium chloride derived from *p*-sulphanilic acid does not appear to form an insoluble compound with antimony trichloride under the above described experimental conditions.

The expenses of this investigation have been defrayed by a grant from the Chemical Society Research Fund.

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CIX.—*Chemical Examination of the Bark of* Euonymus atropurpureus.

By HAROLD ROGERSON.

Euonymus atropurpureus, Jacquin (Nat. Ord. *Celastraceae*), is a shrub indigenous to the northern and western States of North America, where it is known by the common names of "wahoo" and "burning bush." It is frequently cultivated on account of its copious crimson fruit. The root-bark of the plant has been employed to a considerable extent medicinally, and is recognised by both the British and United States Pharmacopœias. A crude, resinous product, as well as an alcoholic extract of the drug, has met with somewhat extended use under the name of "Euonymin," and this appellation has also been given to various other substances obtained from the bark, all of which, however, appear to have been of a very indefinite character.

One of the earliest chemical examinations of *Euonymus* was by Wenzell (*Amer. J. Pharm.*, 1862, **34**, 385), who stated that the bark contained an amorphous, neutral, bitter principle, termed "euonymin," several resins, organic acids, including the so-called "euonic acid," a substance resembling asparagine, sugar, etc. In some notes on the subject by Prescott (*ibid.*, 1878, **50**, 563), the euonymin of Wenzell is referred to as a glucoside, and said to have been obtained by Miller as a white, intensely bitter, uncrystallisable solid, but no further information was given respecting its composition or glucosidic character.

Schmiedeberg (*Arch. exp. Path Pharm.*, 1883, **16**, 163) refers to an hitherto unpublished investigation by Hans Meyer, and records the following statement: "Euonymin.—A glucoside, sparingly soluble in water, but readily in alcohol, which, in amounts of 1/15—1/10 of a milligram, arrests the action of a frog's heart in systole. It crystallises in colourless, cauliflower-like masses, which consist of radiating groups of needles, and is found in small amount in the resinoid of the same name from *Euonymus atropurpureus.*" In a dissertation by G. Romm, Dorpat (*Pharm. Centr-h.*, 1885, **26**, 220), it is also recorded that Meyer had obtained a crystalline glucoside from the bark of *Euonymus atropurpureus*, which agrees in its action with digitalin, and a method was given for its preparation (compare van Ryn, "Die Glykoside," p. 287). The characters of this substance do not appear, however, to have been further determined, since no melting point or analysis was recorded, nor have any facts been noted which would serve to establish its glucosidic nature. It was stated by Romm (*loc. cit.*) that the so-called "euonymin" is contained in larger proportion in the bark of the branches than in that of the root of the above-mentioned species of *Euonymus*, and that there is none of it in *Euonymus europaeus*, Linné.

More recently, Naylor and Chaplin (*Year-book of Pharmacy*, 1889, 405) examined the bark of *Euonymus atropurpureus*, and isolated a crystalline substance melting at about 182°, which they regarded as a glucoside, and designated "atropurpurin." The same authors (*Pharm. J.*, 1889, [iii], **20**, 472) subsequently obtained this substance in a purer form, and found that it was not a glucoside, since it did not reduce Fehling's solution after boiling for three hours with aqueous sulphuric acid. From the results of an analysis it was considered to be "either identical with, or an isomeride of, dulcite." The presence of dulcitol in the bark has since been confirmed by M. Hoehnel (*Pharm. Zeit.*, 1900, **45**, 210).

From the above brief résumé of the literature it will be seen that, with the exception of the occurrence of dulcitol, nothing of a very definite nature has been known regarding the constituents of euonymus bark. It was therefore deemed of interest to subject it to a complete examination, and the results obtained are embodied in the present communication.

EXPERIMENTAL.

The material employed in the present investigation consisted of a good quality of the root-bark of *Euonymus atropurpureus*, Jacquin, which conformed in its characters to the description given in the Pharmacopœias.

As a preliminary experiment, a small quantity (10 grams) of the ground material was tested for the presence of an alkaloid, but with a negative result.

Twenty-five grams of the ground bark were extracted in a Soxhlet apparatus with various solvents, when the following amounts of extract dried at 100° were obtained:

Petroleum	extracted	0·50 gram	=	2·00 per cent.
Ether	,,	0·20 ,,	=	0·80 ,, ,,
Chloroform	,,	0·25 ,,	=	1·00 ,, ,,
Alcohol	,,	3·05 ,,	=	12·20 ,, ,,
Total		4·00 grams	=	16·00 per cent.

For a complete examination of the drug a quantity (22·79 kilograms) of the ground material was thoroughly extracted by continuous percolation with hot alcohol. After removing most of the alcohol, a dark-coloured extract amounting to 7·95 kilograms was obtained.

Distillation of the Extract with Steam. Separation of an Essential Oil.

The above-mentioned extract was subjected to distillation in a current of steam until all the volatile constituents had passed over. The distillate, which contained a small amount of solid substance and some oily drops floating on the surface, was extracted with ether. The ethereal liquid was dried, and the solvent removed, when a small quantity (2·3 grams) of an essential oil was obtained.

The yield of the latter was thus equivalent to 0·01 per cent. of the weight of the drug. On keeping, it deposited a crystalline solid melting at 120°, which evidently was identical with the acid subsequently isolated in much larger amount as described below.

The essential oil, which possessed a pale yellow colour and pleasant odour, distilled between 120° and 160°/25 mm., and gave the colour reaction for furfuraldehyde.

Non-volatile Constituents of the Extract.

After the distillation of the extract with steam as above described, there remained in the distillation flask a dark-coloured aqueous liquid (*A*) and a quantity of a dark brown resin (*B*). These products, when cold, were separated by filtration, and the resin repeatedly washed with hot water until nothing further was removed, the washings being added to the original filtrate.

Examination of the Aqueous Liquid (A).
Isolation of Dulcitol, $C_6H_{14}O_6$.

The aqueous liquid and washings were concentrated under diminished pressure, when, on cooling, a quantity of a crystalline substance separated. This was removed by filtration, and a further amount was obtained by adding alcohol to the liquid. The total amount of solid isolated was 475 grams, which is equivalent to 2·09 per cent. of the weight of ground root-bark employed. A portion of the substance was recrystallised from water with the use of a little animal charcoal, when it was obtained in large, well-defined prisms melting at 186—188°. The aqueous solution was optically inactive. (Found, C = 39·2; H = 7·7. Calc., C = 39·6; H = 7·7 per cent.)

The substance is thus seen to be dulcitol, the occurrence of which in *Euonymus* bark had previously been observed.

In order, however, to further characterise the above-described substance, a quantity of it was acetylated by means of acetic anhydride. The solid obtained on pouring the cooled liquid into water was collected and recrystallised from absolute alcohol, when hexa-acetyldulcitol separated in lustrous, flat needles, melting at 168—169°. (Found, C = 49·5; H = 6·3. Calc., C = 49·7; H = 6·0 per cent.)

The benzoylation of dulcitol has previously been recorded by Bouchardat (*Ann. Chim. Phys.*, 1872, [iv], **27**, 163), who states that the hexabenzoyl derivative melts at 147° and sublimes at 220°. On benzoylating a quantity of the substance by the Schotten-Baumann method, a product was obtained which apparently was not a pure substance. Several other methods were therefore investigated, when the following one was found to give a quantitative yield of hexabenzoyldulcitol: Five grams of pure dulcitol were heated with 70 grams of pyridine, and 30·5 grams of benzoyl chloride gradually introduced. The dulcitol slowly dissolved, and, after boiling for fifteen minutes and cooling, the liquid was poured into water. The precipitated solid was collected and well washed. On recrystallising this product from a mixture of ether and chloroform (equal volumes), the substance separated in well-defined, colourless prisms melting at 189—191° without decomposition. Recrystallisation from the above solvent, or from a mixture of pyridine and alcohol, did not change the melting point of the substance:

0·1892 gave 0·4944 CO_2 and 0·0830 H_2O. C = 71·3; H = 4·9.

$C_{48}H_{38}O_{12}$ requires C = 71·5; H = 4·7 per cent.

Hexabenzoyldulcitol is very soluble in chloroform and pyridine, but only sparingly soluble in ether or boiling alcohol. It is also optically inactive, and does not sublime at 280°. It is therefore evident that the product obtained by Bouchardat (*loc. cit.*) was very impure.

Isolation of a New Acid, Furan-β-monocarboxylic Acid, $C_5H_4O_3$.

After the removal of the dulcitol, as described above, the aqueous liquid was deprived of alcohol by means of a current of steam, and then thoroughly extracted with ether. The ethereal liquid was extracted with aqueous ammonium carbonate, when, on acidifying the alkaline liquid, a quantity of a viscid product was precipitated. This was dissolved in ether, the ethereal liquid being dried and the solvent removed. On keeping the resulting product for some days, a substance was deposited in prismatic needles. This was collected, and, after washing with a little ethyl acetate, recrystallised from water, when a quantity (9 grams) of substance separated in anhydrous laminæ melting at 121—122°:

0·1307 gave 0·2562 CO_2 and 0·0452 H_2O. C = 53·5; H = 3·8.

$C_5H_4O_3$ requires C = 53·6; H = 3·6 per cent.

Two determinations of the molecular weight of the substance, by Barger's microscopic method, gave the following results:

(1) 0·058 in 0·913 ethyl acetate, using benzil as the standard, was between 0·475 and 0·5 mol.

(2) 0·063 in 1·642 alcohol, using azobenzene as the standard, was between 0·32 and 0·30 mol.

(1) Mean M.W. = 130. (2) Mean M.W. = 124.

$C_5H_4O_3$ requires M.W. = 112.

The above-described substance was found to be a monocarboxylic acid, and evidently possesses the formula $C_5H_4O_3$. It is isomeric with pyromeconic acid (m. p. 122°) and with furan-α-carboxylic acid (m. p. 132—133°), but not being identical with either of these substances it is evidently a new compound, and must be *furan-β-carboxylic acid*. It is hoped to confirm this conclusion by the synthesis of the last-mentioned acid.

Furan-β-carboxylic acid is sparingly soluble in cold water, but readily soluble in hot water, ethyl acetate, and alcohol. Its aqueous solution gives no colour with ferric chloride. The acid is volatile in steam, and sublimes at 110°.

Silver Furan-β-carboxylate, $C_5H_3O_3Ag$.—This salt was obtained as a white, granular powder:

0·0888 gave 0·0436 Ag. Ag = 49·1.

$C_5H_3O_3Ag$ requires Ag = 49·3 per cent.

Methyl Furan-β-carboxylate, $C_6H_6O_3$.—This derivative of the acid was prepared by dissolving the latter in methyl alcohol, and saturating the solution with dry hydrogen chloride. It was a colourless liquid, boiling at 160° under the ordinary pressure, and possessed an odour very similar to that of methyl benzoate:

0·1688 gave 0·3512 CO_2 and 0·0768 H_2O. C = 56·7; H = 5·0.

$C_6H_6O_3$ requires C = 57·1; H = 4·8 per cent.

The density and refractive index of methyl furan-β-carboxylate were determined, with the following result:

$$D_{15}^{15} = 1·1744;\ n_D^{20} = 1·46759.$$

It was deemed of interest to compare the above-described constants with those of methyl furan-α-carboxylate (methyl pyromucate), and for this purpose a quantity of the last-mentioned ester was prepared from a pure specimen of pyromucic acid (m. p. 133°). The product was a colourless liquid, boiling at 181° under ordinary pressure, and possessing an odour which slightly resembled that of methyl benzoate. This ester had $D_{15}^{15} = 1·1739$; $n_D^{20} = 1·48599$ (compare Gennari, *Gazzetta*, 1894, **24**, [i], 253).

Stenhouse (Trans., 1872, **25**, 298) has described an acid (m. p. 130°), which he regarded as β-pyromucic acid. This was prepared from an aldehyde obtained from various species of *Fucus*, which he termed "fucusol." No doubt can be entertained, however, that the acid described by Stenhouse was really somewhat impure pyromucic acid.

The original ethereal liquid, after treatment with ammonium carbonate as described above, was extracted with solutions of sodium carbonate and sodium hydroxide respectively, but only traces of amorphous material were thus removed.

Isolation of a New Crystalline Alcohol, Euonymol, $C_{21}H_{30}O_4$.

The ethereal liquid which had been extracted with alkalis, as just described, was dried, and the solvent removed, when a small amount (1·5 gram) of a viscid product was obtained. This product, on keeping, deposited a small quantity (0·5 gram) of a crystalline substance, which was collected and recrystallised from a mixture of ether and ethyl acetate, when it was obtained in prisms melting at 248—250°:

0·1085 gave 0·2888 CO_2 and 0·0871 H_2O. C = 72·6; H = 8·9.

$C_{21}H_{30}O_4$ requires C = 72·8; H = 8·7 per cent.

The above-described compound is thus seen to be an alcohol, which evidently possesses the formula $C_{21}H_{30}O_4$. No substance of this formula having hitherto been described, it must be regarded as a new compound, and, with reference to its properties and the generic name of the plant from which it has been isolated, it is proposed to designate it *euonymol.*

Euonymol possesses a very bitter taste which is more apparent when dissolved in alcohol. If a crystal of the substance be dissolved in a small quantity of acetic anhydride, and a few drops of concentrated sulphuric acid then added, a pink colour is soon developed, which rapidly changes to green, showing a bronze fluorescence, and finally becomes yellow. Euonymol slowly dissolves in sulphuric acid, giving a yellow solution, which shows a brilliant, greenish-yellow fluorescence.

A small quantity of the substance was heated with acetic anhydride, and the resulting product recrystallised from a mixture of ether and ethyl acetate. On cooling, an *acetyl* derivative separated in well-defined, rectangular prisms melting at 215°, but the amount was too small for analysis.

The original aqueous liquid which had been extracted with ether, as described above, was next shaken with chloroform and then with amyl alcohol, but these solvents removed only small amounts of amorphous material, from which nothing definite could be obtained.

The aqueous liquid was distilled in a current of steam in order to remove the amyl alcohol, and, after cooling, was treated with a slight excess of a solution of basic lead acetate. The small amount of precipitate thus produced was collected, washed, suspended in water, and decomposed by hydrogen sulphide. The mixture was filtered, and the filtrate concentrated under diminished pressure to a small volume. This liquid gave a dark brown colour with ferric chloride, but nothing definite could be isolated from it.

The filtrate from the lead precipitate was treated with hydrogen sulphide for the removal of the lead, and, after filtering, was concentrated under diminished pressure to the consistency of a syrup. This contained a quantity of sugar, since it readily reduced Fehling's solution, and yielded *d*-phenylglucosazone melting at 208—209°.

Examination of the Resin (B).

This was a dark brown, soft solid, and amounted to about 730 grams, being thus equivalent to 3·2 per cent. of the drug. It was dissolved in alcohol, mixed with purified sawdust, and the thoroughly dried mixture successively extracted in a Soxhlet apparatus with light petroleum (b. p. 40—60°), ether, chloroform, ethyl acetate, and alcohol.

Petroleum Extract of the Resin.

This was a dark brown mass, which amounted to 460 grams. It was dissolved in ether, and the ethereal liquid extracted successively with aqueous ammonium and sodium carbonates, but nothing was removed by this treatment. The ethereal solution was therefore distilled, and the residue heated in alcoholic solution with an excess of potassium hydroxide. The alcohol was then removed, and, after cooling, water was added and the alkaline liquid thoroughly extracted with ether. The ethereal liquid was dried, and the solvent evaporated, when there remained a quantity (70 grams) of a viscid mass, which became solid on cooling. This was dissolved in a large volume of alcohol, when, on keeping for some days, a quantity (12 grams) of a crystalline product separated in flat needles. On recrystallising this product from a mixture of ethyl acetate and dilute alcohol, it separated in laminæ melting at 135—136°, which gave colour reactions similar to those of the phytosterols.

Isolation of a New Monohydric Alcohol, Euonysterol, $C_{31}H_{51}O\cdot OH$.

The above-described product was found to be a mixture, and, after fractional crystallisation, each fraction was converted into its acetyl derivative, and these recrystallised several times. In this way, small amounts of amorphous material were eliminated. The acetyl derivatives were then hydrolysed with alcoholic potassium hydroxide, and the resulting products recrystallised from a mixture of ethyl acetate and dilute alcohol. The principal fraction consisted of flat needles melting at 137—138°:

0·2494, on heating at 110°, lost 0·0132 H_2O. $H_2O=5·3$.

0·1166 * gave 0·3466 CO_2 and 0·1216 H_2O. $C=81·1$; $H=11·6$.

$C_{31}H_{52}O_2,1\frac{1}{2}H_2O$ requires $H_2O=5·6$ per cent.

$C_{31}H_{52}O_2$ requires $C=81·5$; $H=11·4$ per cent.

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* Anhydrous substance.

A determination of the specific rotatory power gave the following result: 0·2362,* made up to 20 c.c. with chloroform, gave α_D $-40'$ in a 2-dcm. tube, whence $[\alpha]_D$ $-28·2°$.

The above-described substance gave with acetic anhydride and sulphuric acid a colour reaction similar to that produced by the phytosterols, but differs from the latter, inasmuch as it becomes red when moistened with strong sulphuric acid. It also differs from the phytosterols by the presence of two oxygen atoms, although containing but one hydroxyl group. As it is a new compound, it is proposed to designate it *euonysterol.*

Euonysteryl Acetate, $C_{31}H_{51}O_2·CO·CH_3$.—This derivative, when recrystallised from ethyl acetate, separated in laminæ melting at 116—118°:

0·1424 gave 0·4156 CO_2 and 0·1426 H_2O. C = 79·5; H = 11·1.
0·1174 „ 0·3410 CO_2 „ 0·1158 H_2O. C = 79·2; H = 10·9.
$C_{33}H_{54}O_3$ requires C = 79·5; H = 10·8 per cent.

Isolation of a New Monohydric Alcohol, Homo-euonysterol, $C_{40}H_{69}O·OH$.

Although euonysterol represented the chief portion of the previously described mixture, the more soluble acetyl derivative, when decomposed with alcoholic potassium hydroxide, gave a product which separated from a mixture of ethyl acetate and dilute alcohol in laminæ, melting at 133—134°:

0·0997, on heating at 110°, lost 0·0050 H_2O. H_2O = 5·0.
0·0947 * gave 0·2850 CO_2 and 0·1052 H_2O. C = 82·1; H = 12·3.
$C_{40}H_{70}O_2,1\frac{1}{2}H_2O$ requires H_2O = 4·6 per cent.
$C_{40}H_{70}O_2$ requires C = 82·5; H = 12·0 „ „

This compound is evidently a homologue of the previously described alcohol, differing from it by the increment $9CH_2$, and it is therefore proposed to designate it *homo-euonysterol.* Like euonysterol, it became red when moistened with sulphuric acid.

Homo-euonysteryl Acetate, $C_{40}H_{69}O·CO·CH_3$.—This derivative separated from acetic anhydride in leaflets melting at 128—130°:

0·1040 gave 0·3068 CO_2 and 0·1064 H_2O. C = 80·5; H = 11·4.
$C_{42}H_{72}O_3$ requires C = 80·7; H = 11·5 per cent.

Isolation of a New Dihydric Alcohol, Atropurol, $C_{27}H_{44}(OH)_2$.

The original alcoholic mother liquor from the above-described mixture of alcohols was concentrated to about 100 c.c., when, on keeping for a few days, a quantity (2·0 grams) of a crystalline product separated. This was dissolved in a mixture of ethyl acetate and alcohol, when, on cooling, a substance separated in needles melting at 283—285° without decomposition. It was anhydrous, and optically inactive:

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* Anhydrous substance.

0·1196 gave 0·3530 CO_2 and 0·1248 H_2O. C=80·5; H=11·6.
$C_{27}H_{46}O_2$ requires C=80·6; H=11·4 per cent.

This substance gave with acetic anhydride and sulphuric acid, colour reactions similar to those of the phytosterols, but when moistened with sulphuric acid it gave no colour. It is isomeric with homo-olestranol, which was isolated from olive leaves (Trans., 1908, **93**, 901), although not identical with it, and as it does not conform in its properties to any other substance of this formula, it is a new compound. It is therefore proposed to designate it *atropurol*, with reference to the source from which it has been isolated.

Atropuryl Acetate, $C_{27}H_{44}O_2(CO{\cdot}CH_3)_2$.—This was prepared by heating atropurol for some time with acetic anhydride, the product being then crystallised from a mixture of ethyl acetate and alcohol, when it separated in very small needles melting at 169—170°:

0·0938 gave 0·2620 CO_2 and 0·0874 H_2O. C=76·2; H=10·3.
$C_{31}H_{50}O_4$ requires C=76·5; H=10·3 per cent.

The original mother liquors from which the above-described alcoholic substances had been separated yielded on evaporation a viscid product amounting to about 50 grams, but from which nothing definite could be obtained.

Isolation of Citrullol, $C_{22}H_{36}O_2(OH)_2$.

The alkaline, aqueous liquid which had been extracted with ether to remove the unsaponifiable material, as described above, was acidified, when a quantity of fatty acid was precipitated. This was extracted with ether, when a small amount of a sparingly soluble substance was separated by filtration. The latter was crystallised several times from a mixture of pyridine and ethyl acetate, when it was finally obtained in colourless, microscopic needles, melting and decomposing at 285—290°. It gave colour reactions resembling those of ipuranol (*Amer. J. Pharm.*, 1908, **80**, 264, 576) and other similar alcohols. The substance agreed in all its properties with the dihydric alcohol, citrullol, which was first obtained by Power and Moore (Trans., 1910, **97**, 102) from colocynth. (Found, C=71·9; H=10·7. Calc., C=72·1; H=10·4 per cent.)

The diacetyl derivative was prepared by boiling a small quantity of the alcohol with acetic anhydride. It separated from dilute alcohol in leaflets, melting at 164—165°. (Found, C=69·0; H=9·3. Calc., C=69·3; H=9·3 per cent.)

Identification of the Fatty Acids.

The ethereal liquid from which the citrullol had been separated was dried and the solvent removed, when there remained a quantity (320 grams) of a dark-coloured product, consisting of a mixture of fatty acids. A convenient quantity (160 grams) of this product was esterified with methyl alcohol and dry hydrogen chloride, and the methyl esters of the acids distilled under diminished pressure. Two fractions were thus obtained, the first of which passed over between 200° and 230°/15 mm. as a light yellow oil, whilst the second distilled between 240° and 280°/15 mm. as a very viscid, dark yellow oil, which solidified on cooling to a waxy mass.

Fraction 200—230°/15 mm.—This fraction, which was optically inactive and amounted to 105 grams, was hydrolysed with an alcoholic solution of potassium hydroxide, and, after removing most of the alcohol, was diluted with water and exactly neutralised with acetic acid. To the hot liquid an excess of a boiling solution of lead acetate was added, and the precipitated lead salts washed and digested with ether, when a considerable portion was dissolved. The soluble portion of the lead salts yielded 60 grams of liquid acids, whilst the insoluble portion yielded 25 grams of solid acids.

The Liquid Acids.—These acids when distilled under diminished pressure passed over between 215° and 260°/20 mm. as a yellow oil. An analysis and a determination of the iodine value gave the following results:

0·1678 gave 0·4704 CO_2 and 0·1738 H_2O. C=76·5; H=11·5.
0·2304 absorbed 0·3373 Iodine. Iodine Value=146·4.
$C_{18}H_{34}O_2$ requires C=76·6; H=12·1 per cent. I.V.=90·1.
$C_{18}H_{32}O_2$ „ C=77·1; H=11·4 „ „ I.V.=181·4.

It is evident from the above results that the liquid acids consist of a mixture of oleic and linolic acids.

The Solid Acids.—These acids were again converted into their methyl esters, and the resulting product fractionated many times under diminished pressure, when the following fractions were finally obtained: (1) Below 194°; (2) 194—195°; (3) 195—200°; (4) 200—205°; (5) 205—220°/20 mm. The first fraction, after hydrolysis, yielded an acid which, when repeatedly crystallised from ethyl acetate, separated in shining laminæ melting at 62—63°:

0·1295 gave 0·3520 CO_2 and 0·1444 H_2O. C=74·1; H=12·4.
0·1100 neutralised 0·2465 KOH. Neutralisation Value=224·1.

A silver salt of the acid, which was precipitated in three fractions, gave Ag = 29·6, 29·8, and 30·2 respectively:

$C_{16}H_{32}O_2$ requires C = 75·0; H = 12·5; Ag = 29·7 per cent.
Neutralisation Value = 219.

It would appear that this fraction consisted of palmitic acid with a small amount of a lower acid.

Fractions 2, 3, *and* 4 solidified to crystalline masses, and they were separately hydrolysed. The regenerated acids when recrystallised from ethyl acetate separated in laminæ melting at 61—63°, 61—63°, and 60—61° respectively. Each fraction was found by analysis to consist of palmitic acid. (Found, C = 75·0; H = 12·6. C = 74·7; H = 12·5. C = 75·0; H = 12·5 respectively. Calc., C = 75·0; H = 12·5 per cent.)

Fraction 5 did not solidify on long keeping, but deposited a few laminæ on cooling. It was hydrolysed, when palmitic acid (m. p. 60—61°) was obtained, together with a small amount of unsaturated acid.

Fraction 240—280°/15 mm.—This fraction, which amounted to 5 grams, was hydrolysed, and the regenerated acid recrystallised first from alcohol and then fractionally from ethyl acetate. Three fractions were thus obtained, which consisted of shining laminæ melting at 75—76°, 74—76°, and 75—77° respectively. After drying at 110° they were analysed:

0·1486 gave 0·4264 CO_2 and 0·1756 H_2O. C = 78·3; H = 13·1.
0·1002 „ 0·2856 CO_2 „ 0·1194 H_2O. C = 77·7; H = 13·2.
0·1041 „ 0·2970 CO_2 „ 0·1212 H_2O. C = 77·8; H = 12·9.
$C_{26}H_{52}O_2$ requires C = 78·8; H = 13·1 per cent.

It would thus appear that the product from the last-mentioned fraction of esters consisted of cerotic acid, together with some lower acid.

Ether, Chloroform, Ethyl Acetate, and Alcohol Extracts of the Resin.

These extracts were dark crimson masses, amounting to 150, 39, 50, and 30 grams respectively. They possessed a bitter taste, especially the portion soluble only in alcohol. Nothing definite could be obtained from any of them, nor were they glucosidic.

Summary.

The results of the present investigation may briefly be summarised as follows:

The material employed for this investigation consisted of the root-bark of *Euonymus atropurpureus*, Jacquin. An alcoholic extract of this material when distilled in a current of steam yielded an amount of a pale yellow essential oil equivalent to 0·01 per cent. of the weight of the drug.

The portion of the extract which was soluble in water contained a quantity of dulcitol amounting to 2·09 per cent. of the weight of the drug; a new acid, $C_5H_4O_3$, melting at 121—122°, which evidently is *furan-β-carboxylic acid*; a new crystalline alcohol, $C_{21}H_{30}O_4$ (m. p. 248—250°), which has been designated *euonymol*; and a sugar which yielded *d*-phenylglucosazone (m. p. 208—209°), together with small amounts of tannin and colouring matter.

The portion of the extract which was insoluble in water consisted of a dark brown resin amounting to 3·2 per cent. of the weight of the drug. From this resin the following substances were isolated: Three new alcohols, namely: *Euonysterol*, $C_{31}H_{51}O{\cdot}OH$ (m. p. 137—138°; $[\alpha]_D - 28{\cdot}2°$); *homoeuonysterol*, $C_{40}H_{69}O{\cdot}OH$ (m. p. 133—134°); *atropurol*, $C_{27}H_{44}(OH)_2$, melting at 283—285°; citrullol, $C_{22}H_{36}O_2(OH)_2$, which has previously been obtained from colocynth (Trans., 1910, **97**, 102); and a mixture of fatty acids consisting of palmitic, cerotic, oleic, and linolic acids.

In the course of this investigation no product could be obtained corresponding with the "euonymin" described by Schmiedeberg (*Arch. exp. Path. Pharm.*, 1883, **16**, 163), and subsequently by Romm (*Pharm. Centr-h.*, 1885, **26**, 220) as a crystalline glucoside, which is stated to have been isolated by Hans Meyer from the bark of *Euonymus atropurpureus*. Moreover, there was no evidence of the presence of any glucosidic substance in the bark.

In conclusion, the author wishes to express his warmest thanks to Dr. F. B. Power for having suggested this research, and for the very kind interest he has manifested in the investigation; to Mr. F. H. Lees, F.I.C., for determining the refractive indices of methyl furan-α- and β-carboxylates; and to Mr. A. J. Ewins, B.Sc., for determining the molecular weight of furan-β-carboxylic acid by the microscopic method.

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CX.—*The Constituents of West Indian Satinwood.*

By SAMUEL JAMES MANSON AULD and SAMUEL SHROWDER PICKLES.

Two varieties of satinwood come into commerce, distinguished as East Indian and West Indian, the former being derived from *Chloroxylon Swietenia*, D.C., and the latter from *Zanthoxylum* *flavum*, Vahl. (*Fagara flava*, Kr. et Urb.). They are both used in the manufacture of furniture, the latter in much greater quantity than the former. On several occasions there have been complaints from workmen using satinwood that it produced severe skin eruptions, and articles by medical men who have come in contact with cases of skin irritation produced by satinwood have been published from time to time in the *British Medical Journal* (Jones, June 25th, 1904; Bidie, January 14th, 1905; Graham, April 15th, 1905).

In the Annual Report of the Chief Inspector of Factories for 1907 it was made clear that all the outbreaks which have occurred so far were due to East Indian satinwood, and up to the present no trouble has been reported as arising from the use of the West Indian variety.

Some time ago the attention of the Imperial Institute was directed to this question, and the investigation of both kinds of satinwood was undertaken in the Scientific and Technical Department. The results of the chemical examination of the constituents of East Indian satinwood and the isolation of an active alkaloid by one of us have already been published (Auld, Trans., 1909, **95**, 964). The investigation of the pharmacological action of the East Indian wood and of the constituents above mentioned was undertaken by Prof. J. T. Cash, F.R.S., of Aberdeen University, and his results have also recently been published (*Brit. Med. J.*, October 7th, 1911; *Bull. Imp. Inst.*, 1911, **9**, 351).

The present paper deals with the examination of the constituents of West Indian satinwood, which, although probably not responsible for the causation of skin irritation, may, according to Prof. Cash (*loc. cit.*), contain constituents which are capable of continuing or even reproducing the dermatitis once this has been set up in a subject by the action of the East Indian wood.

In order to facilitate extraction, the wood was first reduced to sawdust. About 1500 grams of the ground material were extracted in the first instance with light petroleum (b. p. below 50°), afterwards with 90 per cent. alcohol, and finally with boiling water.

Light Petroleum Extract.

On concentrating the petroleum solution a quantity of crystalline material separated in large, cauliflower-like rosettes, consisting of needle-shaped prisms. It was almost colourless, but contained yellow patches, which were apparently due to the presence of a coloured, viscous oil. The oil was drained off as far as possible, and the solid material was pressed on a porous tile and recrystallised from methyl alcohol, from which it separated in aggregates of prismatic needles (m. p. 124—126°), which were almost colourless. This substance dissolves in concentrated sulphuric acid with the production of a red coloration, and on the addition of water is reprecipitated unchanged. It contains no nitrogen, and on analysis gave the following results:

(1) 0·1595 gave 0·4060 CO_2 and 0·0775 H_2O. C=69·4; H=5·4.
(2) 0·1447 „ 0·3685 CO_2 „ 0·0710 H_2O. C=69·45; H=5·45.
$C_{11}H_{10}O_3$ requires C=69·47; H=5·26 per cent.

It is very sparingly soluble in boiling water, giving a neutral solution, from which it is reprecipitated on cooling. The substance dissolves with difficulty in potassium hydroxide solution, and on continued boiling the solution becomes yellow. It is reprecipitated from the alkaline solution on the addition of acids. The general behaviour of this substance seems to indicate a lactonic character, and it is found that many other compounds occurring in this and closely allied woods are of a similar nature (compare Priess, *Ber. Deut. pharm. Ges.*, 1911, **21**, 227). It was thought that it might possibly be a phytosterol, but on examination it gave none of the characteristic reactions of this group of compounds. The substance absorbs bromine, and is unsaturated.

In spite of the ease with which this substance crystallises and gives a fairly constant melting point, indications were observed, which lead the authors to suspect the presence along with it, of a second compound very similar in composition and in properties. Up to the present, however, no satisfactory separation has been effected.

The yellow oil referred to above was very small in quantity, and on keeping for some time partly solidified. It was obviously a mixture, and was not further examined.

Alcoholic Extract.

After the removal of the remaining light petroleum, the ground wood was extracted with 90 per cent. alcohol, first by cold, and afterwards by hot, percolation.

In each case the alcohol was carefully distilled off under diminished pressure, and the combined residues were extracted with very dilute warm hydrochloric acid. This was repeated until the acid washings no longer gave a reaction with iodine solution.

The acid solution after separation was rendered alkaline with ammonia and shaken with ether. On evaporation the ethereal solution left a resinous residue, which was redissolved in dilute hydrochloric acid. The solution was filtered, rendered just alkaline again with ammonia, extracted with ether, and the ethereal solution evaporated. A very small quantity of alkaloidal residue was thus obtained, which gave reactions with the usual alkaloid reagents, but which was too impure and too small in quantity to admit of characterisation.

The resinous residue remaining after the treatment with dilute acid was redissolved in alcohol, and the fairly concentrated solution allowed to remain. A large quantity of a yellow, crystalline material separated, which was removed, washed with alcohol, and dried on a porous plate. It was then recrystallised from alcohol and several times from ethyl acetate, the solution being boiled each time with animal charcoal. The substance was finally obtained in large, translucent, rhombic prisms having a sulphur-yellow colour, which could not be removed by recrystallisation. It melted sharply at 133°. The crystals are quite different from those deposited from the light petroleum extract, and a mixture of the two showed a considerable depression of the melting point.

The pale yellow compound, melting at 133°, has a faint, but distinct, coumarin-like odour, very noticeable on warming. It sublimes about 110°, and condenses again in crystals. It is readily soluble in alcohol, chloroform, or hot ethyl acetate, sparingly so in ether, but almost insoluble in boiling water or light petroleum.

The following results were obtained on analysis of material which had been boiled for one and a-half hours with animal charcoal in alcoholic solution, and afterwards crystallised six times from absolute alcohol:

0·1525 gave 0·4125 CO_2 and 0·0690 H_2O. C=73·77; H=5·03.
0·2040 „ 0·5520 CO_2 „ 0·0940 H_2O. C=73·80; H=5·12.
$C_{14}H_{12}O_3$ requires C=73·7; H=5·3 per cent.

The molecular weight of the compound was determined by the cryoscopic method in benzene.

Found: M.W.=217, 240, 240. Mean, 232.
$C_{14}H_{12}O_3$ requires M.W.=228.

This compound, $C_{14}H_{12}O_3$, is apparently a pure, well-defined substance, and the following experiments were made with the idea of determining its nature.

The fact that it contained three oxygen atoms suggested the possible presence of reactive hydroxyl or carboxyl groups, but these are apparently absent.

On boiling a small quantity of the substance with acetic anhydride and sodium acetate for two hours, no change was effected, the original material being afterwards recovered.

In the crystalline condition the compound is practically insoluble in water and also in aqueous potassium hydroxide, although when finely divided (powdered) it dissolves slowly in the latter on prolonged boiling, a yellow-coloured solution being produced.

When heated on the water-bath with alcoholic potassium hydroxide the substance gave a deep yellow solution. After boiling for two hours and subsequently distilling off the alcohol, the original compound was regenerated on the addition of an acid.

This behaviour towards potassium hydroxide suggests the splitting of a lactone ring, rather than the presence of a carboxyl group in the molecule.

An attempt to prepare an oxime by treating the compound with hydroxylamine hydrochloride and potassium hydroxide gave a negative result, and similar attempts to prepare a semicarbazone and phenylhydrazone were also unsuccessful.

The absence of methoxyl groups in the compound was proved by a Zeisel determination.

Since there are no hydroxyl, carboxyl, methoxyl, aldehydic, or ketonic groups present in the compound, and as it cannot be an ester, the conclusion was formed that the substance must be an ether-lactone.

Action of Bromine.

The compound $C_{14}H_{12}O_3$ contains one double bond. In a preliminary experiment, 0·562 gram dissolved in chloroform and treated with bromine (also in chloroform solution) until the brown colour just remained absorbed approximately 0·42 gram. A compound having the above formula and containing one ethylenic linking should absorb 0·40 gram of bromine.

For the preparation of the dibromide it is necessary that moisture should be carefully excluded. A small quantity of the substance melting at 133° was dissolved in chloroform, the solution cooled in a freezing mixture, and to it was slowly added a solution of bromine in chloroform until the bromine was just in excess. Light petroleum was then added to the chloroform solution. At first a small quantity of viscid, resinous material separated. The solution was poured off from this, and more petroleum was added, when the dibromide separated in small, colourless, prismatic needles melting at 125°:

0·1685 gave 0·1620 AgBr. Br = 41·01.

$C_{14}H_{12}O_3Br_2$ requires Br = 41·2 per cent.

Action of Water on the Dibromide.

The dibromide is almost immediately decomposed by water, with the formation of hydrogen bromide and a monobromohydroxy-compound:

$$C_{14}H_{12}O_3Br_2 + H_2O = C_{14}H_{12}O_3Br{\cdot}OH + HBr.$$

A solution of the dibromide in alcohol is neutral towards litmus, but if a few drops of water are added it becomes acid in reaction owing to the liberation of hydrogen bromide. For the preparation of the monobromohydroxy-compound a small quantity of the dibromide was boiled with water for a few minutes. The solid material was then collected and dried on a porous plate. On crystallising from dilute acetic acid it was obtained in small, colourless crystals melting at 168—169°:

0·1990 gave 0·1162 AgBr. Br = 24·84.

$C_{14}H_{13}O_4Br$ requires Br = 24·62 per cent.

Acetate of the Monobromohydroxy-compound.

A small quantity of the above compound was boiled with acetic anhydride and sodium acetate for two hours. The resulting acetyl compound was separated by pouring the solution into water, and after recrystallisation from dilute acetic acid was obtained in slender, colourless needles melting at 152°:

0·1665 gave 0·835 AgBr. Br = 21·5.

$C_{16}H_{15}O_5Br$ requires Br = 21·8 per cent.

Fusion with Potassium Hydroxide.

The crystalline material (m. p. 133°; 5 grams) was mixed with potassium hydroxide (20 grams) and a little water in a nickel dish, and fused for about half an hour, the temperature being kept below 250°. A considerable quantity of a gaseous substance having an odour like benzene or toluene escaped, and burned with a luminous flame. The fusion, after cooling, was dissolved in water, acidified, and submitted to steam distillation.

The distillate was neutralised with dilute potassium hydroxide solution, concentrated almost to dryness, and acidified with sulphuric acid, when a strong butyraceous odour was observable. The acid liquors were extracted with ether, and on evaporation of the ether the residue was neutralised with ammonia, and concentrated silver nitrate solution was added. Analysis showed that this was the silver salt of butyric acid. (Found, M.W. = 89·4. Calc., M.W. = 88.)

The non-volatile portion of the acidified fusion consisted of a mixture of phenolic substances, from which no definite compound has yet been isolated.

Oxidation Experiments.

By the oxidation of a small quantity of the substance (dissolved in acetic acid) with chromium trioxide there were obtained (1) a pale yellow, neutral, crystalline compound (m. p. 174°), and (2) an acid which was present in the oxidation products in the form of a chromium salt. The acid was liberated on acidifying with sulphuric acid, and extracted with ether, from which solution on evaporation it was obtained in colourless crystals. It was recrystallised from alcohol, and then melted at 204—206°. It gave a purple coloration with ferric chloride solution, and was at first thought to be β-resorcylic acid. On mixing a little with the latter acid, however, it was found that the melting point was reduced to 196°, and further, the acid obtained as above gave no coloration with bleaching powder solution.

On oxidation of another portion of the substance (m. p. 133°) in alcoholic solution with potassium permanganate, a pale yellow substance almost insoluble in ether was obtained. This dissolved in alcohol, from which solvent it was deposited in pale yellow plates melting at 212—213°.

It is a saturated compound which slowly dissolves in solutions of the alkalis with a deepening of the yellow colour, and is therefore probably the dihydroxy-derivative, $C_{14}H_{10}O_3(OH)_2$.

A further portion of the substance was treated with nitric acid (D 1·2), and boiled under a reflux condenser until the solution was almost colourless. On subsequent extraction with ether and chloroform, there was obtained a mixture of nitrated compounds, one of which melted at 237°, and a pale yellow, crystalline substance, melting at 210—212°. Under more severe conditions the nitric acid oxidation produced mainly oxalic acid, but with acid of 15—20 per cent. strength a small quantity of colourless, crystalline material was produced. This was obtained in needles melting at 205—206° on recrystallisation from alcohol. On re-melting, it fuses at 126°, and gives a fluorescein with resorcinol. It is therefore possibly phthalic acid, although there was not sufficient material for confirmation.

Examination of the Resins.

After removing as much material as was possible by crystallisation from alcohol, the solvent was evaporated off. There remained a viscid, clear brown, resinous substance having a peculiar burning taste, which developed on the tongue only after some time. This effect was also accompanied by a choking sensation at the back of the throat.

Endeavours were made to isolate the constituent to which these effects were due. The resins as a whole had no action on the skin of the forearm or under the armpit when applied directly externally.

On treating the resin with dilute potassium hydroxide solution it was found that a considerable portion dissolved, and from taste tests it was apparent that the portion which caused the tingling effect was amongst the alkali-soluble constituents. Since, however, there are probably many substances present, it was found necessary to apply other methods, and after many experiments the following scheme of separation was adopted.

Treatment with Sodium Carbonate.

An alcoholic solution of the resins was warmed with excess of a solution of sodium carbonate in dilute alcohol. A portion dissolved in the alkaline liquid, and a partial separation was effected. This process was repeated several times.

The solution was acidified with dilute sulphuric acid, and the precipitate obtained was redissolved in alcohol, and again precipitated by adding water. There was thus obtained a soft brown resin (A^2), which was practically devoid of the tingling taste of the crude resin.

The residue was well washed with water, and then dissolved in strong alcohol. A quantity of sodium carbonate separated, which was removed. Water was then added to the alcoholic solution, and the precipitate was washed again with water and redissolved in alcohol.

Treatment with Barium Hydroxide.

To this solution was then added a saturated alcoholic solution of barium hydroxide. A yellow precipitate separated; this was collected, washed, and warmed to 50—60° with dilute sulphuric acid to decompose the barium compounds. The aqueous liquor was then drained off, and the residue was washed, dried, and extracted with alcohol. On adding water to the alcoholic solution, a semi-solid resin was precipitated. This was designated B^2, and it had the pungent taste of the crude resin.

Treatment with Lead Acetate.

The solution from which the barium compounds had been separated was afterwards freed from excess of barium hydroxide by passing carbon dioxide through it, and subsequent filtration. A concentrated solution of lead acetate in 90 per cent. alcohol was added in excess, when a dense precipitate was obtained. This precipitate was washed, suspended in water, and hydrogen sulphide was passed through the mixture. The black precipitate containing lead sulphide was extracted with alcohol, the extract was concentrated somewhat, and water was added to the hot liquid until turbid. The solution was allowed to cool, when a brown, powdery, non-pungent resin (C^2) separated. The mother liquor from this was then diluted with more water to ensure complete precipitation, and by this means a yellow precipitate was obtained, which on drying gave a powdery resin (D^2). This was also without the tingling effect on the tongue.

The filtrate from the lead acetate precipitate was freed as far as possible from lead by treatment first with carbon dioxide and afterwards with hydrogen sulphide, and, after filtration, the clear solution was evaporated and poured into water, when a resinous precipitate separated (resin E^2).

Precipitation from Chloroform Solution.

This was dried, dissolved in chloroform, and to the solution so obtained light petroleum (3 vols.) was added.

This caused the precipitation of a further resin fraction (F^2). This was solid and slightly pungent.

The chloroform–petroleum solution on keeping deposited a quantity of almost colourless, crystalline matter melting at 112—114° (crystalline compound No. 3), which had a marked pungent taste.

Precipitation from Benzene.

The solvent was then evaporated off, and the residue, by solution in benzene and subsequent precipitation with light petroleum, was finally separated into two fractions: (1) a viscid, crystalline solid (F^3), and (2) a pale yellow, viscous resin (F^4), which also showed a tendency to crystallise. Both of these had the marked pungent taste.

Specimens of the crystalline compounds and of the above resins have been sent to Prof. Cash, of Aberdeen University, and are at present under investigation for their pharmacological properties.

Extraction of the Wood with Water.

After complete extraction of the sawdust with alcohol the remaining alcohol was removed, and the wood extracted with boiling water.

The extract thus obtained was evaporated almost to dryness, extracted with water, filtered, and to the filtrate alcohol was added, which caused the separation of a precipitate. On drying, this became tough and friable, and was apparently pectous matter.

The filtrate from this precipitate contained tannin, but nothing further of a definite character was isolated.

SCIENTIFIC AND TECHNICAL DEPARTMENT,
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CXI.—*Researches on Santalin. Part I. Santalin and its Derivatives.*

By JOHN CANNELL CAIN and JOHN LIONEL SIMONSEN.

RED sanderswood (*Pterocarpus santalinus*, L.) (also known as saunders-wood, sandal wood, and santal wood) is found principally in Ceylon and Southern India, and is imported into England for dyeing purposes. The rasped dyewood is used chiefly in wool dyeing; it gives red shades on an aluminium or tin mordant, and is used in conjunction with other dyewoods, for example, logwood, old fustic, etc., for the purpose of obtaining various shades of brown, olive, drab, etc. Its use, however, is limited, as the shades produced are not fast to light or alkalis.

The colouring matter, santalin, contained in the wood has been isolated and analysed by various chemists, but as widely differing formulæ have been put forward as representing its composition it seemed of interest to prepare the pure dyestuff, to analyse it, and to investigate its constitution.

Santalin was first analysed by Pelletier (*Ann. Chim. Phys.*, 1832, [ii], **51**, 193), who gave it the formula $C_{16}H_{16}O_5$. Then Bolley (*Annalen*, 1847, **62**, 150) assigned to it the formula $C_{27}H_{26}O_9$, Weyermann and Häffely (*Annalen*, 1850, **74**, 226) found $C_{15}H_{14}O_5$, and finally Franchimont and Sicherer (*Ber.*, 1879, **12**, 14) the formula $C_{17}H_{16}O_6$.

It will be observed that Bolley's formula differs only very slightly from that found by Weyermann and Häffely, and no doubt for this reason this formula for santalin is given in Gmelin's "Handbuch" (where a full list of the earlier literature is to be found). Further, a careful reading of the literature affords certain indications as to the weight to be attached to the above chemists' results. The material obtained by Bolley was amorphous, and became tarry at 100°. L. Meier (*Arch. Pharm.*, 1848, **55**, 285; **56**, 41), who prepared the dyestuff but did not analyse it, found its melting point to be 104°; the substance, however, contained ash. Weyermann and Häffely took care to remove inorganic impurity by treating the alcoholic solution of the dyestuff with hydrochloric acid, and finally obtained a red, crystalline powder which could be dried at 100°, but no melting point is given. It seems probable, therefore, that their product melted, at any rate, above 104°.

Franchimont and Sicherer stated that they obtained a product free from ash by boiling the precipitated dyestuff with dilute hydrochloric acid (in which it is insoluble), but that the material obtained was not crystalline and melted at 104—105°. It would appear from the above that the purest material was obtained by Weyermann and Häffely, and we may state at once that our work confirms this conclusion in that the pure dyestuff prepared by us is free from ash, forms a red, crystalline powder, and melts at 226°. Further, our analyses point to the conclusion that the formula $C_{15}H_{14}O_5$, put forward by Weyermann and Häffely, is the correct one.

We have also found that if a trace of organic impurity (tarry matter) is left in the material (as at various stages of its purification), the melting point is depressed to about 104°, but the carefully purified dyestuff melts at the higher temperature.

With regard to the constitution of santalin practically nothing is known. Weyermann and Häffely analysed the lead and barium salts, giving them the formulæ $C_{15}H_{12}O_5Pb$ and $C_{15}H_{13}O_5,\frac{1}{2}Ba$ respectively. A. G. Perkin (Trans., 1899, **75**, 443) described the potassium salt, $C_{15}H_{13}O_5K,C_{15}H_{14}O_5$, and Brooks (*Philippine J. Sci.*, 1910, **5**, 449) the copper salt, $(C_{15}H_{13}O_5)_2Cu$. Franchimont and Sicherer fused the dyestuff with potassium hydroxide, and obtained acetic acid, resorcinol, and probably protocatechuic acid and catechol. By oxidation with potassium permanganate in alkaline solution they detected oxalic and acetic acids, and observed an odour of vanillin, but could not isolate this compound; on oxidation with nitric acid they detected oxalic acid and either picric or styphnic acid. Finally, the presence of one methoxyl group was indicated.

The saplings of *Pterocarpus santalinus*, when freshly gathered, are quite colourless, and contain free sugar and a *glucoside*, which on hydrolysis decomposes into a *phlobaphen* and dextrose, whilst the wood of the tree, which is red, contains free santalin (compare von Cochenhausen, *Zeitsch. angew. Chem.*, 1904, **17**, 883). We have isolated the pure colouring matter from (*a*) the wood as grown in India, (*b*) the rasped wood as imported into England, and (*c*) the commercial dyestuff (Merck). As already mentioned, the formula is $C_{15}H_{14}O_5$, and it contains one methoxyl group.* As it forms a *diacetyl* derivative (contrary to Franchimont and Sicherer's statement), from which *nitrodiacetylsantalin* was prepared, and a *dibenzoyl* derivative, the presence of two hydroxy-groups is indicated. Santalin forms an *oxime*, a *nitro-* and a *benzeneazo*-derivative. When treated with methyl sulphate it furnishes the *dimethyl ether*, together with a *compound*, the constitution of which is yet unknown. When the dimethyl ether is oxidised, it yields veratric and anisic acids, and when *nitrosantalin*

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* See Cain and May, *7th. Int. Congr. Appl. Chem.*, London, 1909, IV *B*, 85.

dimethyl ether is oxidised it gives anisic acid and a substance which is probably a nitroveratric acid.

EXPERIMENTAL.

Examination of the Saplings of Pterocarpus santalinus.

In view of the suggestion of von Cochenhausen (*loc. cit.*) that santalin occurs in the plant as a glucoside, a careful examination of the sapling was made.

The saplings investigated by the authors were freshly gathered, and were quite free from any trace of colour except at the end of the stem where they had been attached to the tree. Even on keeping for several months in a hot climate no sign of change of colour due to hydrolysis was to be observed. As the following experiments show, the saplings undoubtedly contain a glucoside and free sugar; there was only a trace of an essential oil present.

The finely divided wood (100 grams) was extracted several times with an excess of hot alcohol, when a pale brown solution was obtained, which, on cooling, deposited a small amount of a colourless, amorphous solid (not further examined). After filtration, the alcoholic solution was concentrated to about 100 c.c., and treated with excess of lead acetate solution, when a voluminous, white precipitate separated. This was collected, well washed with hot alcohol, and the filtrate reserved for later investigation. The lead salt was suspended in hot alcohol and decomposed with hydrogen sulphide, and after filtration the alcohol was removed, when a viscid, colourless oil (6 grams) was obtained, which rapidly darkened on exposure to the air. This oil was evidently a glucoside, but it could not be obtained in crystalline form. It readily reduced Fehling's and silver solutions, and gave with ferric chloride a bright green coloration, which rapidly darkened with separation of a greenish-brown precipitate.

Hydrolysis of the Glucoside.—The crude glucoside (1 gram) was mixed with dilute sulphuric acid (10 c.c. of a 1 per cent. solution), and heated for some hours on the water-bath. A white solid almost immediately separated, but in a short time it changed colour and became red, whilst the whole solution also assumed a red colour. After cooling, the red solid was collected, and the filtrate reserved for examination for the presence of a sugar.

The red solid obtained in this way was evidently a *phlobaphen.* It is very sparingly soluble in all organic solvents, and resisted all attempts to crystallise it. When mixed with dilute potassium hydroxide it gave a sage-green coloration, which rapidly turned brown and then red; the main portion of the solid did not dissolve, and was apparently not phenolic. When fused with potassium hydroxide it yielded only protocatechuic acid and an oil which had a strong odour of butyric acid.

The filtrate from which the phlobaphen had been separated was treated with barium carbonate, and after removal of the barium sulphate and unchanged carbonate was concentrated on the water-bath, when a viscous oil was obtained. This oil on treatment with phenylhydrazine in the usual manner gave an osazone which showed all the properties of glucosazone.

The filtrate from the lead salt of the glucoside was treated with hydrogen sulphide to remove excess of lead, and after filtration was evaporated to dryness. The brown oil (5 grams) was extracted with water, when the main portion (3 grams) was found to consist of an insoluble resin, which was not further examined. The aqueous solution gave a copious precipitate of glucosazone on treatment with phenylhydrazine. There can, therefore, be little doubt that the wood contains sugar in the free state; it is interesting to observe that after keeping the wood for some months during the hot weather this sugar completely disappeared.

Extraction and Purification of Santalin.

The santalin made use of in these experiments was obtained from three different sources, namely, (1) by direct extraction of the red heart wood of the *Pterocarpus santalinus*, (2) by extraction from the rasped wood as imported into England, and (3) by purchase from Merck.

(1) *Extraction of* Pterocarpus santalinus.—For the purpose of these experiments a very fine specimen of this wood was obtained for us by Dr. J. R. Henderson, Superintendent of the Madras Museum. The red heart wood was separated, and after being converted into fine sawdust was extracted with boiling alcohol until no further colouring matter was removed. The deep red alcoholic solution was concentrated, and lead acetate solution was added until no further precipitate was formed, the solution boiled, and allowed to remain for some hours. The crude lead salt of santalin which was obtained in this manner was collected, well washed with hot alcohol, and decomposed with hydrogen sulphide. After removing the lead sulphide, the alcoholic solution of the colouring matter was concentrated and precipitated by water. A viscid, red oil was thus obtained, which slowly solidified when ground with water. It was collected, and after drying was further purified by conversion into its sparingly soluble potassium salt by the method described by A. G. Perkin (*loc. cit.*). The colouring matter was recovered

from the potassium salt, repeatedly crystallised from dilute alcohol, and dried at 100°:

0·1326 gave 0·3177 CO_2 and 0·0686 H_2O. C = 65·4; H = 5·7.
$C_{15}H_{14}O_5$ requires C = 65·7; H = 5·1 per cent.

The yield of santalin obtained in this manner is variable. In one set of experiments 950 grams of the wood yielded 68 grams of crude santalin.

(2) *Extraction of the Wood imported into England.*—For the extraction and purification of the dye from the wood (which was kindly supplied to us by the British Dyewood and Chemical Co., Ltd., Bury, Lancashire), Meier's process of extraction was combined with Weyermann and Häffely's method of purification. The rasped wood is extracted with ether, the ethereal solution evaporated, and the residue boiled with water until the extract, at first yellow, becomes pale red. At this stage the solid, previously tarry, can be powdered with the finger. It is dissolved in 80 per cent. alcohol, precipitated with an alcoholic (80 per cent. alcohol) solution of lead acetate, the lead salt collected, and boiled several times with 80 per cent. alcohol until the filtrate is colourless. The lead salt is then suspended in 80 per cent. alcohol, heated with dilute sulphuric acid, the solution filtered from lead sulphate, and precipitated with water. The gelatinous mass is heated with a little sodium chloride, filtered, dissolved in 80 per cent. alcohol, and the solution boiled with dilute hydrochloric acid; if this treatment is omitted, the product is found to contain ash. The dye is now precipitated with water, and crystallised from 80 per cent. alcohol, from which it separates as a microcrystalline cake. The yield of crude dye was about 16 per cent. of the wood, as has been stated by previous investigators, and the amount of pure substance obtained was about one-fifth of the crude material. In one experiment the dye, precipitated with water, was boiled with dilute hydrochloric acid, as recommended by Franchimont and Sicherer (*loc. cit.*), but after this treatment it still contained ash:

0·1732 gave 0·4174 CO_2 and 0·0804 H_2O. C = 65·7; H = 5·1.
0·1808 „ 0·146 AgI. OMe = 10·7.*
0·2580, in 17·12 of phenol, gave $\Delta t = -0·44°$. M.W. = 257.†
$C_{14}H_{11}O_4{\cdot}OMe$ requires C = 65·7; H = 5·1; OMe = 11·3 per cent.
M.W. = 274.

(3) *From Merck's Santalin.*—During the later experiments it was found more convenient to prepare the santalin from Merck's commercial product. For the purpose of purification it was sufficient

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[*] For this analysis, we are indebted to Dr. Clarence Smith.

[†] Mr. Percy May kindly carried out this determination.

to convert it into the potassium salt, the operation being repeated twice. One specimen was purified by crystallisation from dilute alcohol and analysed:

0·1124 gave 0·2696 CO_2 and 0·0578 H_2O. C = 65·4; H = 5·7 per cent.

Santalin when prepared by either of these methods is obtained as a bright red, microcrystalline powder. It softens at 223°, and melts to a deep red oil at 226°. It is readily soluble in alcohol or acetic acid, but only very sparingly so in benzene, toluene, or light petroleum. It dissolves in alkalis with a deep red colour, whilst its alcoholic solution gives immediate precipitates with potassium, barium, and copper salts. The potassium salt, $C_{15}H_{13}O_5K,C_{15}H_{14}O_5$, prepared from potassium acetate gave K = 6·58. Calc., K = 6·67 per cent. (compare A. G. Perkin, Trans., 1899, **75**, 443). When dissolved in acetic acid and treated with bromine, santalin yields a *bromo*-derivative, but so far we have not succeeded in obtaining it in a pure state. Santalin is also oxidised with great readiness by nitric acid, and even with very dilute acid only oxalic acid could be isolated from the oxidation products; on the other hand, ozone has no action on it.* When boiled with phenylhydrazine no reduction takes place.†

Derivatives of Santalin.

Diacetylsantalin, $C_{19}H_{18}O_7$.—Santalin (2 grams) was dissolved in acetic anhydride (25 c.c.), and after the addition of a few drops of pyridine the mixture was boiled for one hour. In another experiment 1 gram of santalin was boiled with 5 grams of acetic anhydride for three hours. The cooled, deep red solution was poured into water, and after the acetate had solidified it was collected, repeatedly crystallised from hot alcohol and finally from amyl alcohol, and dried at 130°:

0·1341 gave 0·3121 CO_2 and 0·0606 H_2O. C = 63·5; H = 5·0.
0·501 „ 0·1641 $C_2H_4O_2$.‡ $CH_3{\cdot}CO = 23{\cdot}47$.
$C_{15}H_{12}O_5(CH_3{\cdot}CO)_2$ requires C = 63·7; H = 5·0;
$CH_3{\cdot}CO = 24{\cdot}02$ per cent.

Diacetylsantalin is a reddish-brown, microcrystalline powder melting at 216—218° when slowly heated. It is only sparingly soluble in cold alcohol, but more readily so in the boiling solvent, or in hot amyl alcohol or acetic acid.

In order to make certain that no molecular change had taken place in the preparation of this substance, it was hydrolysed, and the santalin was recovered unchanged. (Found, C=65·6; H=5·5. Calc., C=65·7; H=5·1 per cent.)

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* Dr. Isherwood kindly tried this experiment for us.

† We are indebted to Prof. A. G. Green for making this experiment.

‡ By A. G. Perkin's method (Proc., 1904, **20**, 171).

Reducing Acetylation of Santalin.—Santalin (1 gram) was mixed with sodium acetate (1 gram), zinc dust (2 grams), and acetic anhydride (10 c.c.) The mixture was heated on the sand-bath for five hours, when the deep red colour of the solution had become much paler in shade. After filtering, the cold solution was poured into water, and the pale brown solid which separated was collected and dried. In order to obtain the acetate in a pure state, it was first boiled with absolute alcohol, in which only a little impurity is dissolved, and then crystallised once from dilute acetic acid and dried at 100°:

0·1447 * gave 0·3353 CO_2 and 0·0663 H_2O. C=63·3; H=5·1.
$C_{21}H_{20}O_8$ requires C=63·0; H=5·0 per cent.

It would appear from the analysis that three acetyl groups had entered the molecule of santalin. The compound separates from acetic acid as a pale brown powder, which sinters at 232° and melts at 242—245°.

Nitrodiacetylsantalin, $C_{19}H_{17}O_9N$.—Diacetylsantalin (2·3 grams) was dissolved in acetic anhydride (5 c.c.), and a mixture of nitric acid (D 1·4; 2 c.c.) in acetic anhydride (5 c.c.) was added gradually with constant cooling. The mixture was allowed to remain overnight, and then poured into water, when a reddish-brown solid separated. This was collected, dried, and purified by repeated crystallisation from acetic acid. After being dried at 110°:

0·1155 gave 0·2395 CO_2 and 0·0469 H_2O. C=56·5; H=4·5.
0·1537 „ 5·1 c.c. N_2 at 29° and 766 mm. N=3·6.
$C_{19}H_{17}O_9N$ requires C=56·5; H=4·2; N=3·5 per cent.

Nitrodiacetylsantalin is a bright scarlet, microcrystalline powder. It has no melting point, but blackens at about 270°.

Dibenzoylsantalin, $C_{15}H_{12}O_5Bz_2$.—Santalin (1 gram) was dissolved in pyridine (15 grams), and to the well-cooled solution benzoyl chloride (11·5 grams) was gradually added. After remaining in the cold overnight, the mixture was poured into water, when a red oil was obtained. Considerable difficulty was experienced in making this oil solidify, and ultimately it was found best to dissolve it in acetic acid and precipitate it fractionally with water, when a brown powder was obtained. It was purified by repeated crystallisation from dilute acetic acid, and dried at 110°:

0·1124 gave 0·2986 CO_2 and 0·0501 H_2O. C=72·4; H=4·9.
$C_{29}H_{22}O_7$ requires C=72·2; H=4·6 per cent.

Dibenzoylsantalin has so far only been obtained in the form of an amorphous, brownish-red powder, which sinters at 173° and melts at 180—181°. It is only sparingly soluble in alcohol or amyl alcohol, but more readily so in acetic acid or ethyl acetate.

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* Ash=0·0002.

Santalinoxime.—For the preparation of this substance the method recently devised by Lapworth and Steele (Trans., 1911, **99**, 1884) was used. Santalin (1 gram) was dissolved in absolute alcohol (50 c.c.), and anhydrous sodium acetate (1 gram) and hydroxylamine hydrochloride (0·4 gram) were added. The mixture was heated for four hours on the water-bath, poured into water, and the flocculent precipitate collected.

The *oxime* was purified by repeated separation from dilute alcohol, when it was obtained as an amorphous, red powder. It does not melt at 270°:

0·1722 * gave 0·3867 CO_2 and 0·0831 H_2O. C = 61·6; H = 5·3.
0·1683 „ 6·9 c.c. N_2 at 30° and 762 mm. N = 4·3.
$C_{15}H_{15}O_5N$ requires C = 62·3; H = 5·2; N = 4·8 per cent.

Benzeneazosantalin,† $C_6H_5 \cdot N_2 \cdot C_{15}H_{13}O_5$, prepared by treating an alkaline solution of santalin with benzenediazonium chloride, is a purple powder which does not melt. It dissolves very slowly in aqueous potassium hydroxide to a brownish-red solution, and gives a reddish-brown coloration with sulphuric acid.

Found: N = 7·3. $C_{21}H_{18}O_5N_2$ requires N = 7·4 per cent.

The Methylation of Santalin.

In view of the importance of the methyl ether of santalin for oxidation experiments, the methylation of santalin under various conditions was most carefully investigated. Under all conditions *santalin dimethyl ether*, $C_{14}H_9O_2(OMe)_3$ (m. p. 165—167°), was isolated, but at the same time another product was also obtained, the nature of which has not so far been elucidated.

(1) In one experiment santalin (20 grams) was dissolved in aqueous potassium hydroxide (8 grams of potassium hydroxide in 40 c.c. of water), and with constant cooling and shaking methyl sulphate in excess was gradually added, care being taken that the solution was kept just alkaline. The bright red colour of the solution slowly changed, became much browner, and an oily solid separated. When the reaction was complete the solution was treated with excess of potassium hydroxide, and boiled to destroy any unchanged methyl sulphate. On cooling, the crude methyl ether (15 grams) was collected and dried.

The purification of the methyl ether is a matter of considerable difficulty. The crude substance is boiled with a large volume of alcohol, when the main quantity dissolves, leaving a small amount of an insoluble residue (*A*). This was separated, and the deep red solution allowed to remain, when a quantity of a bright red solid separated. This was collected and mixed with *A*. The mother liquor was concentrated, and if nothing further separated the solution was fractionally precipitated with water, and the semi-solid fractions were ground with water until solid. The melting points of these various fractions were taken, and all those which melted above 180° were placed on one side and mixed with *A*.

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* Ash = 0·0008.

† For the preparation of this compound we are indebted to Dr. Clarence Smith.

The portions of lower melting point were mixed together and purified by repeated crystallisation from dilute alcohol, when ultimately a microcrystalline, red powder of constant melting point was obtained and dried at 110°:

0·1116 gave 0·278 CO_2 and 0·0612 H_2O. C = 67·9; H = 6·1.*
0·1684 „ 0·4032 AgI. OMe = 31·6.
$C_{14}H_9O_2(OMe)_3$ requires C = 67·5; H = 5·9; OMe = 30·8 per cent.

Santalin dimethyl ether prepared in this manner melts at 165—167°, and further crystallisation does not raise this. It is readily soluble in alcohol, acetic acid, or ethyl acetate, but is only sparingly so in benzene or light petroleum. It is not acted on by alcoholic potassium hydroxide, even on long boiling.

The sparingly soluble substance *A* which was separated during the purification of the methyl ether was crystallised from amyl alcohol, when it was obtained as a microcrystalline, red powder sintering at 235° and melting at 248—250°. It has not so far been obtained free from ash. After drying at 110°, it gave analytical figures agreeing moderately well with those required for santalin monomethyl ether, but the proof of its identity with that substance must be reserved for a future communication:

0·1164 † gave 0·2742 CO_2 and 0·0577 H_2O. C = 65·6; H = 5·6.
0·1493 „ 0·2624 AgI. OMe = 23·2.
$C_{16}H_{16}O_5$ requires C = 66·6; H = 5·5; OMe = 21·5 per cent.

When santalin is methylated in this manner it yields approximately 9 grams of the methyl ether and 5 grams of the substance melting at 248—250°.

(2) If santalin is methylated in alcoholic solution it is found that a much larger yield of the substance melting at 248—250° is obtained, the yield of the dimethyl ether being correspondingly diminished. In one such experiment santalin (40 grams) was dissolved in alcohol, and after the addition of methyl sulphate

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* Other analyses gave C = 67·8, H = 6·2; C = 67·3, H = 5·9.

† Ash = 0·0024.

(60 grams), sodium hydroxide (20 grams of sodium hydroxide in 30 c.c. of water) was gradually added, the solution being well cooled. When all reaction had ceased, the same amounts of methyl sulphate and sodium hydroxide were added. The methyl derivatives began to separate out as a viscid oil, and after remaining overnight water was added and the product collected. After fractional crystallisation from alcohol as described above, 10 grams of santalin dimethyl ether and 27 grams of the other product were obtained.

(3) In order to determine if one of the hydroxy-groups present in santalin was situated in the α-position with respect to a carbonyl group, santalin (2 grams) was mixed with sodium (0·5 gram), dissolved in methyl alcohol (100 c.c.), and after the addition of methyl iodide (6 grams) the mixture was heated at 100° for three hours in a sealed tube. After cooling, the reaction mixture was poured into water, the solid collected, and separated as previously described, when santalin dimethyl ether (10·6 grams) and the substance melting at 248—250° were isolated.

Oxidation of Santalin Dimethyl Ether.

As the result of a number of comparative experiments the following fairly satisfactory method was employed for the oxidation of santalin dimethyl ether and the separation of the products.

The ether (22 grams) was ground to a fine powder, and made into a thin paste with water and dilute sodium carbonate solution. The mixture was placed in an apparatus fitted with an automatic stirring arrangement, and gradually treated with a 5 per cent. solution of potassium permanganate. The oxidation proceeded slowly, and when about 40 grams of permanganate had been added, the pink colour was permanent. The mixture was then heated on the water-bath, when further oxidation took place, and was not complete until approximately 75 grams of potassium permanganate had been added. The solution was separated from the manganese dioxide, the latter well washed with boiling water, and the combined filtrate concentrated to a small bulk. The pale brown solution was acidified and distilled in a current of steam, when a small amount of a neutral oil passed over, and the distillate had a strong odour of a fatty acid.

Examination of the Steam Distillate.—The steam distillate was saturated with ammonium sulphate, and repeatedly extracted with ether. The ethereal extract was washed with dilute sodium carbonate solution, dried, and the ether evaporated, when a trace of neutral oil was obtained; the quantity was, however, too small for examination. The sodium carbonate washings were acidified and extracted with ether. On evaporation of the ether a small quantity of an oil was obtained, which had the characteristic odour of butyric acid. The silver and calcium salts were prepared and analysed. (Found: Ca=19·3 and Ag=55·4. Calc., Ca=18·7 and Ag=55·4 per cent.)

As the result of these analyses there can be little doubt that the acid is butyric acid, but the yield is so small that it is in all probability produced by some side reaction.

Examination of the Residue from the Steam Distillate.—The aqueous residue from the steam distillation contained a viscid, red oil. This was treated with ether, when a small amount of resinous matter remained undissolved. The ethereal solution was dried and evaporated, and the residual oil allowed to remain for some time in a vacuum desiccator. Crystallisation slowly occurred, and after some days the semi-solid mass was drained on porous porcelain.* The purification of the mixture of acids thus obtained was a matter of considerable difficulty, and it was only after a long series of experiments that the following method was devised and found to give fairly satisfactory results.

The acids were dissolved in hot benzene, the solution concentrated and allowed to remain overnight, when a quantity had separated as crystalline nodules (*A*). These were separated, and the mother liquor was further concentrated, when a second crop of crystals (*B*) was obtained. When no further crystallisation took place, the benzene was removed, and the slightly oily acid (*C*) which separated was again drained on porous porcelain.

The first fraction (*A*) was repeatedly crystallised from hot water, when it was obtained in needles which melted sharply at 178°, and showed all the properties of veratric acid. (Found, C=59·2; H=5·5. Calc., C=59·3; H=5·5 per cent.) The identity of this acid was further confirmed by the mixed melting-point method and by the preparation of the methyl ester melting at 57—58°.

The fractions *B* and *C* were now subjected to fractional crystallisation from hot water, when ultimately two main fractions were obtained, that of higher melting point (about 165°) consisting of fairly pure veratric acid, whilst the second fraction melted quite sharply at 145°. Owing to the constancy of its melting point, this acid was for a long time thought to be a pure substance, and was analysed (C=60·1; H=5·4). On treatment, however, with dilute nitric acid it was ultimately found possible to separate it into veratric and anisic acids.

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* The porous plates from several such oxidations were extracted with ether, the recovered acids esterified and the esters distilled under diminished pressure, when it was found that practically the whole passed over at 190—210°/36 mm. The mixture of esters was hydrolysed, and the solid acids obtained were separated as described above.

The acid melting at 145° (0·6 gram) was mixed with nitric acid (D 1·25; 10 c.c.), allowed to remain in the cold for ten minutes, and then heated on the water-bath, first at 70—80° for ten minutes and finally at 100° for five minutes. The acid slowly dissolved, the solution becoming pale yellow. The mixture was cooled, when a colourless, crystalline solid was deposited; water was added, and the solid and solution dissolved in ether. The ethereal solution was washed with sodium carbonate solution, dried, and evaporated, when a yellow solid remained which melted at 93—94° and evidently consisted of nitroveratrole.

The sodium carbonate washings were acidified and again extracted with ether, and on removal of the ether a yellow solid remained. This was crystallised from hot water, when, on rapid cooling, a colourless acid separated in fine needles. These were again crystallised from hot water, and after drying at 100° were found to melt at 181°, shrinking at 180·5°. When mixed with anisic acid melting at 181·5°, the melting point was 181—182°, the mixture shrinking slightly at 180°. There can therefore be little doubt that this acid is anisic acid. (Found, C=62·8; H=6·1. Calc., C=63·2; H=5·2 per cent.) Further confirmation that the acid obtained was a mixture of anisic and veratric acids was afforded by a study of the melting-point curve of mixtures of these acids, the lowest temperature recorded being 142·5°. An equimolecular mixture of the acids melted at 144°. This mixture was recrystallised from water; the crystals melted at 145°, and the filtrate, on evaporation, gave a residue which melted at 142·5°. The crystals melting at 145° were again recrystallised from water, and the product melted at the same temperature. When mixed with a specimen of the acid obtained by the oxidation of santalin dimethyl ether, no change of melting point was observed. Further, from the melting-point curve the composition of the mixture melting at 145° would be 37 per cent. of anisic acid and 63 per cent. of veratric acid, which requires C=60·6; H=5·4, agreeing well with the figures given above.

From the mother liquors from which the anisic acid was isolated, a yellow solid was obtained, crystallising in rosettes of needles and melting at 187°; this was found to be nitroveratric acid. A comparative experiment showed that anisic acid was not nitrated under the conditions employed.

Nitrosantalin Dimethyl Ether.

Nitrodiacetylsantalin was hydrolysed by treating it with a slight excess of aqueous sodium hydroxide. The deep brown solution was kept for fifteen minutes, cooled, and treated with a large excess of methyl sulphate. Nitrosantalin dimethyl ether separated out during the process as an oil, which rapidly solidified. It was collected, purified by crystallisation from acetic acid, and dried at 110°:

0·1298 gave 4·5 c.c. N_2 at 30° and 764 mm. N=3·8.

$C_{17}H_{17}O_7N$ requires N=4·1 per cent.

Nitrosantalin dimethyl ether has so far only been obtained in the form of a brown, amorphous powder. It does not melt at 300°, but gradually blackens.

The yield of this compound was extremely poor, and it was necessary to recover the partly methylated material from the alkaline mother liquors and treat it once more with alkali and methyl sulphate in order to obtain sufficient of this substance for our experiments.

Oxidation of Nitrosantalin Dimethyl Ether.

The following method was used to oxidise nitrosantalin dimethyl ether, but as the yield obtained was very poor it is obviously capable of considerable improvement.

The substance (10 grams) was finely powdered, suspended in dilute sodium carbonate solution, and gradually treated with potassium permanganate solution (5 per cent.). A slight rise in temperature took place, and after the addition of 400 c.c. of the permanganate solution the reaction became very slow and was completed by heating to 100° in the water-bath, a further 600 c.c. of the permanganate solution being added. The manganese dioxide was separated, and the pale yellow solution concentrated. On acidification a yellow oil was precipitated, which was extracted with ethyl acetate, the solution being dried and evaporated. The residual brown oil was esterified with alcohol and sulphuric acid, and the ester isolated in the usual manner. About 2 grams of a viscid, brown oil were thus obtained, and this was subjected to distillation under diminished pressure (40 mm.). A small amount of a colourless oil passed over at 190—200°, the remainder distilling irregularly between 200° and 260°, leaving a very considerable residue in the flask.

The fraction boiling at 190—200°, which weighed only 0·2 gram, was hydrolysed, and the resulting acid isolated in the usual manner. The oil thus obtained rapidly solidified, and after draining on porous porcelain was crystallised from hot water, in which a portion was only very sparingly soluble. This was separated, and the acid crystallised from the filtrate in glistening needles, which after two crystallisations melted sharply at 179—180°, and this melting point was not altered when the acid was mixed with anisic acid.

The sparingly soluble acid, which weighed only a few milligrams, was purified by crystallisation from a mixture of benzene and ethyl acetate, when it was obtained in small, yellow plates melting at 212°. It was nitrogenous, but no further examination was possible.

The ester of high boiling point (200—260°) was a viscid, yellow oil, and slowly crystallised in rosettes of needles. These were drained on porous porcelain and purified by crystallisation from alcohol, when the ester was obtained in long, yellow needles melting at about 141°. Owing to the small amount of material at our disposal we were not able to obtain it in a pure state, but it is possible that it is the ester of a nitroveratric acid, since it was nitrogenous, and gave the following results on analysis:

Found: $C=50{\cdot}6$; $H=5{\cdot}5$.

$C_{11}H_{13}O_6N$ requires $C=51{\cdot}8$; $H=5{\cdot}1$ per cent.

We propose to subject these oxidation products to a more detailed examination in order to gain further information as to the constitution of santalin.

In conclusion, we desire to express our thanks to the Research Fund Committee for a grant which partly defrayed the cost of the above investigation, and also to Dr. J. R. Henderson, Superintendent of the Madras Museum, for his assistance in obtaining for us the saplings and specimens of the wood.

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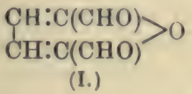
CXII.—*Furan-2 : 5-dialdehyde.*

By William Francis Cooper, B.A.(Cantab.), and
Walter Harold Nuttall, F.I.C.

Fenton and Robinson (Trans., 1909, **95**, 1339) have shown that when ω-chloromethylfurfuraldehyde is oxidised by nitric acid, a very energetic reaction takes place, and dehydromucic acid (furan-2:5-dicarboxylic acid) is produced. Alberda van Ekenstein and Blanksma (*Ber.*, 1910, **43**, 2361) state that ω-hydroxymethylfurfuraldehyde on similar treatment gives dehydromucic acid.

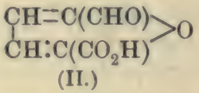
While preparing a large quantity of this acid by Fenton and Robinson's method, the present authors observed that the yield varied within wide limits; and on investigating the cause of this variation, it was noticed that the reaction product often contained a substance or substances extractable with organic solvents, such as benzene and chloroform, in which dehydromucic acid is practically insoluble. The chloroform extract, after drying, left a crystalline residue on evaporation.

This has been found to consist of furan-2:5-dialdehyde (I) mixed with a small quantity of a white, crystalline substance, which combines the properties of an aldehyde and an acid. It is most probably identical with furan-2-aldehyde-5-carboxylic acid (pyromucic aldehyde) (II) described by Hill and Sawyer (*Amer. Chem. J.*, 1898, **20**, 174), who obtained it by the hydrolysis with water of ω-dibromomethylpyromucyl bromide, prepared by the bromination of methylpyromucyl chloride. Hill and Sawyer give 201—202° as the melting point of their compound; the white, crystalline compound referred to above melts at 196—197°. A slight impurity would probably explain this difference, but, unfortunately, the yield was too small to enable the identity to be confirmed by analysis:



$$\left.\begin{array}{l}\mathrm{CH{:}C(CHO)} \\ \mathrm{CH{:}C(CHO)}\end{array}\right>\mathrm{O}$$

(I.)



$$\left.\begin{array}{l}\mathrm{CH{=}C(CHO)} \\ \mathrm{CH{:}C(CO_2H)}\end{array}\right>\mathrm{O}$$

(II.)

Furan-2:5-*dialdehyde* (I) has not been previously prepared, and, as the analogue of glyoxal, is a compound of interest and worthy of description.

Furan-2:5-dialdehyde shows all the usual properties of an aldehyde. It gives a diphenylhydrazone, a dianilide, and a dioxime. No attempt has yet been made to prepare the stereoisomerides of the oxime. An attempt to prepare the monoxime by the use of one equivalent of hydroxylamine hydrochloride gave the dioxime only. This behaviour is exactly analogous to that of glyoxal.

In addition to the above, the derivative with β-naphthylamine has also been prepared and analysed; as this reagent appears to be very suitable for the identification of aldehydes of the furan series. The β-naphthylamine derivatives are easily prepared, are crystalline, and the melting points of the various compounds differ more widely than those of other derivatives. The following have been prepared and their melting points determined for purpose of identification:

	M. p.
β-Naphthylamine derivative of furfuraldehyde	85° *
,, ,, methylfurfuraldehyde	87—88°
,, ,, ω-hydroxymethylfurfuraldehyde	131—132°
,, ,, furan-2:5-dialdehyde	Above 230°

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* Schiff, *Annalen*, 1887, **239**, 350.

The constitution of the dialdehyde follows from its mode of preparation, as well as from its easy conversion into dehydromucic acid by oxidation with silver oxide. Attempts to reduce it to 2:5-dihydroxymethylfuran, or to prepare it by the reduction of the methyl ester of dehydromucic acid, were not successful.

In common with other furanaldehydes, the dialdehyde gives striking colours on condensing with phenols, etc., by means of concentrated sulphuric acid. The most characteristic of these is the reaction with thymol. Addition of a few drops of concentrated sulphuric acid to a solution of the dialdehyde and thymol in alcohol produces a brilliant magenta colour. A large excess of acid changes this into a beautiful Prussian blue. On pouring into water, the colour changes into red, and a red dye is precipitated. The formation of the blue colour distinguishes the dialdehyde from other furanaldehydes, and, as it is extremely delicate, forms a convenient test for the new compound. A solution of 1 part of the dialdehyde in 50,000 parts of water gives the blue colour. The aldehyde acid gives a red colour with thymol, but the blue is not produced with excess of sulphuric acid.

As an analogue of glyoxal, the compound would be expected to polymerise readily, and investigations on this and other reactions are being made.

In addition to some dehydromucic acid, other products of the oxidation of ω-chloromethylfurfuraldehyde are oxalic acid and a very considerable quantity of hydrocyanic acid. Other oxidising agents, such as potassium dichromate in acid solution, may be used instead of nitric acid. The authors have also obtained the dialdehyde by the restrained oxidation of ω-hydroxymethylfurfuraldehyde by nitric acid (D 1·3). During this investigation they have discovered a simplified method of preparation of ω-hydroxymethylfurfuraldehyde, which is described later.

Fenton and Gostling (Trans., 1899, **75**, 430) first obtained ω-hydroxymethylfurfuraldehyde from ω-bromomethylfurfuraldehyde by precipitating in dilute alcoholic solution with slightly more than the calculated quantity of silver nitrate. Free nitric acid, which might conceivably have an oxidising action on the aldehyde, being produced by this method, Erdmann (*Ber.*, 1910, **43**, 2392) recommended the substitution of silver acetate for the nitrate. Fenton and Gostling further showed that ω-hydroxymethylfurfuraldehyde can be prepared by the hydrolysis of the corresponding bromo-compound with water in presence of barium carbonate. The present authors have since shown, however (Trans., 1911, **99**, 1195), that this hydrolysis is not a simple one; a yellow, crystalline compound, $C_{11}H_{10}O_4$, is produced, the constitution of which has not yet been determined, and, at the same time, there is a corresponding reduction in the yield of the hydroxy-aldehyde. The authors have found that a satisfactory method of preparing this aldehyde is by the hydrolysis of ω-chloromethylfurfuraldehyde by simply pouring the crude product into a large mass of almost boiling water, when hydrolysis results immediately; the hydroxy-aldehyde passes into solution, and may be extracted with ethyl acetate. If the volume of water is large, the concentration of hydrogen chloride liberated is not sufficiently great to react with the hydroxy-aldehyde. The method is not applicable to the bromo-analogue, as the liberated hydrogen bromide does react with the hydroxy-aldehyde.

EXPERIMENTAL.

*Preparation of Furan-*2:5-*dialdehyde.*

Fifty grams of crude ω-chloromethylfurfuraldehyde, prepared by a slight modification of the method described by Fenton and Robinson (Trans., 1909, **95**, 1339), namely, by the action of hydrogen chloride on lævulose, are treated with 100 c.c. of concentrated nitric acid (D 1·3) in a large flask. The mixture is heated gently, with constant shaking, until the reaction commences, when the flask is immediately immersed in cold water. Even then the reaction is very violent, brown oxides of nitrogen and hydrogen cyanide being copiously evolved. When the reaction has subsided, the contents of the flask are diluted with water, filtered from a small quantity of brown, insoluble matter, and extracted with benzene or chloroform—preferably the latter. The extract is dried over ignited sodium sulphate, and the solvent distilled off from a water-bath; the dark, residual oil, on cooling, quickly solidifies to a brown mass of crystals, which consist of the dialdehyde mixed with a small quantity of the aldehyde-acid. The yield of the crude mixture varies between 25 and 30 per cent. of the theoretical. A partial separation of the dialdehyde and aldehyde-acid can be brought about by recrystallisation from carbon tetrachloride, in which the aldehyde-acid is only very sparingly soluble, and from which the dialdehyde crystallised in light yellow, thin plates. Complete separation, however, can only be accomplished by boiling the aqueous solution with barium carbonate, when the barium salt of the aldehyde-acid is produced and passes into solution. The aqueous solution is extracted with chloroform to remove the dialdehyde, after which the aldehyde-acid may be extracted from the residual liquid after acidification.

The dialdehyde can be conveniently purified by recrystallisation from carbon tetrachloride, but the solvent clings very tenaciously to the product.

It can be obtained in beautiful, feathery, iridescent plates from light petroleum containing about 2 per cent. of chloroform. From chloroform or ether it crystallises in characteristic aggregates, having the upper surface flat and the lower globular. Under the microscope these are found to consist of layers of extremely thin, waxy, transparent plates. The substance melts at 109·5—110° (uncorr.).

For the analysis, the substance, after several recrystallisations from carbon tetrachloride, was crystallised once from ether, and dried under diminished pressure over sulphuric acid:

0·1823 gave 0·3886 CO_2 and 0·0558 H_2O. C=58·13; H=3·40.
0·1333 in 20·1 benzene gave $\Delta t = -0{\cdot}263°$. M.W.=126·1.
0·1110 „ 21·74 „ „ $\Delta t = -0{\cdot}206°$. M.W.=123·9.
$C_6H_4O_3$ requires C=58·06; H=3·23 per cent. M.W.=124.

It is somewhat soluble in water, readily so in alcohol, ether, ethyl acetate, or benzene, and extremely so in chloroform; it does not dissolve in light petroleum. It is easily volatile in steam, and also in the vapours of chloroform and benzene. It sublimes below 100° in a most characteristic manner; the sublimate resembles cotton-wool, and when viewed under the microscope this is found to consist of aggregations of glistening plates.

The compound cannot be conveniently purified by this method, as the unsublimed portion rapidly liquefies and darkens, probably due to polymerisation.

The compound quickly colours Schiff's reagent, and readily reduces ammoniacal silver nitrate or Fehling's solution on warming. It dissolves easily in cold aqueous sodium hydroxide or barium hydroxide, forming an acid, as it cannot be extracted from these solutions by organic solvents.

It is also soluble in ammonium hydrate (D 0·880), giving a brown solution, from which a flocculent precipitate soon separates.

No hydrogen sulphite compound could be obtained.

Besides the colour with phenols, already described, the dialdehyde gives a beautiful blue when condensed with dimethylaniline by heating with zinc chloride.

With anthraquinone and concentrated sulphuric acid an olive-green colour is obtained.

The Phenylhydrazone.—Four grams of the dialdehyde were dissolved in ethyl acetate, and 9 grams (rather more than 2 mols.) of phenylhydrazine, also in ethyl acetate, were added. After the addition of anhydrous potassium carbonate, the mixture was boiled and filtered, and part of the solvent removed by distillation. Petroleum of high boiling point was added to the residue, when the *phenylhydrazone* separated as a yellow, crystalline precipitate. It was purified by recrystallisation from benzene containing a little methyl alcohol, when it melted at 206—207° (uncorr.):

0·1817 gave 0·4733 CO_2 + 0·0908 H_2O. C = 71·04; H = 5·55.
0·2549 „ 41·0 c.c. N_2 (moist) at 15° and 748 mm. N = 18·5.
$C_{18}H_{16}ON_4$ requires C = 71·05; H = 5·26; N = 18·4 per cent.

The Dianilide.—Two grams (1 mol.) of the dialdehyde were triturated with 3 grams (2 mols.) of aniline. The aldehyde soon dissolved, and the warm mixture quickly solidified. Excess of ether was added, and the insoluble anilide collected. Four grams of crude anilide were obtained, and this was purified by crystallisation from absolute alcohol, from which it separated in light yellow, glistening plates melting at 160—161° (uncorr.). The alcoholic solution on boiling readily gave a red dye:

0·3645 gave 32·2 c.c. N_2 (moist) at 18° and 758 mm. N = 10·2.
$C_{18}H_{14}ON_2$ requires N = 10·2 per cent.

The Di-β-naphthylamine Derivative.—Three grams of the dialdehyde in alcohol were added to 9 grams of β-naphthylamine, also in alcohol. There was an immediate, yellow, crystalline precipitate, which, as the mixture became heated, changed to red. It was collected and washed, first with alcohol and afterwards with ether, when it was obtained in glistening, golden-yellow plates. It was purified for analysis by extraction with alcohol, and drying the residue in a vacuum desiccator. It is a yellow, crystalline solid, almost insoluble in the ordinary organic solvents with the exception of glacial acetic acid:

0·3722 gave 24·5 c.c. N_2 (moist) at 16° and 752 mm. N = 7·6
$C_{26}H_{20}ON_2$ requires N = 7·4 per cent.

The Dioxime.—Four grams of the dialdehyde were dissolved in warm 50 per cent. alcohol, 4·4 grams of hydroxylamine hydrochloride (2 mols.) added and dissolved, and finally 6·2 grams of anhydrous potassium acetate were dissolved in the mixture. The substance crystallised out immediately on cooling in very fine needles radiating from a common nucleus and melting at 212·5—213° (uncorr.). For analysis it was recrystallised from dilute methyl alcohol and dried at 95°:

0·2183 gave 33·9 c.c. N_2 (moist) at 18° and 769 mm. N = 18·2.
$C_6H_6O_3N_2$ requires N = 18·2 per cent.

Attempt to Prepare the Monoxime.—Two grams of the dialdehyde were dissolved in 50 per cent. alcohol and heated with 1·1 grams of hydroxylamine hydrochloride (1 mol.) and 1·6 grams of anhydrous potassium acetate in the manner described in the preparation of the dioxime. The solution darkened somewhat, and on cooling gave a good crop of yellowish-brown crystals.

These crystallised from water in characteristic, microscopic, flat, dentate needles radiating from a common point, and melting at 212—213°. Analysis showed that this compound was the dioxime.

Oxidation of the Dialdehyde to Dehydromucic Acid, $C_6H_4O_5$.

For this purpose the dialdehyde was heated with excess of freshly precipitated well washed silver oxide and water for three hours on a boiling-water bath. After removing the silver oxide, the soluble silver was precipitated with a slight excess of hydrochloric acid, and the filtrate therefrom concentrated to a small bulk. After several hours the acid crystallised out.

As considerable difficulty was experienced in purifying the acid directly, it was converted into its barium salt, which was recrystallised twice from water, and then the acid regenerated from it by exact precipitation with sulphuric acid. It was thus obtained in shining, white plates. (Found, C=46·10; H=2·74. Calc., C=46·15; H=2·56 per cent.)

The acid does not melt below 220°; it sublimes easily, and gives the characteristic red jelly on warming with ferric chloride solution.

β-Naphthylamine Derivative of Methylfurfuraldehyde.

The methylfurfuraldehyde was prepared by the reduction of ω-bromomethylfurfuraldehyde by means of stannous chloride (Fenton and Gostling, Trans., 1901, **79**, 811). The crude aldehyde so obtained was triturated with slightly more than two parts of well powdered β-naphthylamine. The mixture became warm, and quickly solidified. The mass was extracted with ether, in which the required derivative is very soluble, filtered, and the crystalline residue therefrom recrystallised from 50 per cent. alcohol. Soft, almost white, microscopic needles separated, which melted at 87—88° (uncorr.). The compound is very readily soluble in all the usual organic solvents. After being dried over sulphuric acid:

0·5925 gave 30·5 c.c. N_2 (moist) at 16·5° and 760 mm. N=6·0.

$C_{16}H_{13}ON$ requires N=6·0 per cent.

β-Naphthylamine Derivative of ω-Hydroxymethylfurfuraldehyde.

One part of ω-hydroxymethylfurfuraldehyde dissolved in ethyl acetate was mixed with slightly more than one part of β-naphthylamine, also in ethyl acetate. The mixture was boiled with anhydrous potassium carbonate, and filtered. After the removal of most of the solvent by distillation, the residue solidified on cooling. The crystals were collected, washed with ethyl acetate, dissolved in benzene, and precipitated by the addition of light petroleum. On recrystallisation from heavy petroleum, yellow, glistening, flat needles were obtained, which melted at 131—132° (uncorr.). After being dried in a vacuum:

0·6112 gave 30·0 c.c. N_2 (moist) at 21° and 768 mm. $N=5·7$.

$C_{16}H_{13}O_2N$ requires $N=5·6$ per cent.

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CXIII.—*Studies on Platinocyanides.*

By LEONARD ANGELO LEVY, M.A.

THE investigation of platinocyanides presents many points of especial interest owing to the many unique and peculiar properties of this interesting class of compounds. The remarkable play of colours and dichroism displayed by the crystalline salts, the fluorescence exhibited by them under the stimulation of various types of radiation, and the formation of numerous multi-coloured hydrates are all properties which are practically confined to these substances. Some observations on the conditions which determine their property of fluorescence and also on the existence of isomeric crystalline modifications of some of these salts, have already been published (Trans., 1908, **93**, 1446). Two interesting examples of multi-coloured hydrate formation have also been described (Trans., 1906, **89**, 125). The observations which are set forth below, whilst they do not follow directly on former experiments, are the results of some investigations on the oxidation products of platinocyanides, a subject with regard to which there appears to be a considerable difference of opinion.

The action of the halogens and of nitric acid on potassium platinocyanide was first investigated by Weselsky (*Sitzungsber. K. Akad. Wien*, 1856, **20**, 282; *J. pr. Chem.*, 1856, **69**, 276) and by Knop (*Annalen*, 1842, **43**, 111). They obtained products in the form of needle-shaped crystals with a marked metallic, coppery lustre, to which the formula $M_2Pt(CN)_5$ was assigned. Hadow subsequently reinvestigated the subject, and obtained results totally different from those of the earlier chemists. The composition represented by the formula $M_2Pt(CN)_5$ is questionable for the following reasons:

(1) The platinum and basic metal remain in the same ratio as in the original platinocyanide. The difference between the two classes of salts is merely a variation in the content of cyanogen. It is therefore necessary to assume that the platinum and basic metal are removed in equal proportions by the oxidising agent.

(2) The salts act as oxidising agents in the presence of potassium hydroxide, platinocyanide being regenerated. If the formula $M_2Pt(CN)_5$ correctly represented the composition of these substances, the following equation would express the reaction:

$$2M_2Pt(CN)_5 + 2KOH + M = 2M_2Pt(CN)_4 + 2KCN + MO + H_2O,$$

that is, the solution should contain free cyanide, of which, however, it shows no trace.

Hadow proved that the ratios between the platinum, basic metal, and cyanogen were the same as in the platinocyanides. The copper-coloured oxidation products were shown to be platinocyanides, to which a proportion of halogen was added. He further showed that the compounds could be regarded as double salts of platinocyanide and the completely halogenated platinocyanide. The formula $5K_2Pt(CN)_4,K_2Pt(CN)_4X_2,18H_2O$ (where X is an atom of halogen) was assigned to them. This composition was verified by the synthetical production of the copper-coloured salt from potassium platinocyanide and potassium perchloro(or bromo)-platinocyanide.

Hadow's investigations were very conclusive, and it might reasonably have been expected that they settled definitely the question of the constitution of the compounds under consideration. Such, however, does not appear to be the case. That a difference of opinion still exists may be gathered from the following extracts:

The following paragraph is taken from the English translation of Mendeléeff's "Principles of Chemistry" (1905, p. 409): "By the action of chlorine or dilute nitric acid, the platinocyanides are converted into salts of the composition $M_2Pt(CN)_5$, which correspond with $Pt(CN)_3,2KCN$. . . . The potassium salt of this series, $K_2Pt(CN)_5,3H_2O$, forms regular, brown prisms with a metallic lustre, and is soluble in water, but insoluble in alcohol. Alkalis reconvert this compound into the ordinary platinocyanide, $K_2Pt(CN)_4$, taking up the excess of cyanogen. Under the action of excess of chlorine, a solution of potassium platinocyanide gives, besides $K_2Pt(CN)_5$, a product, $K_2Pt(CN)_4Cl_2$, which evidently contains the form PtX_4, but at first the action of chlorine produces an easily soluble intermediate salt which crystallises in thin copper needles. It apparently corresponds to

$$5K_2Pt(CN)_4,K_2Pt(CN)_4Cl_2,24H_2O."$$

Mention has also been made (*Proc. Roy. Soc.*, 1909, *A*, **82**, 380) of a salt to which the formula $Li_2Pt(CN)_5,3H_2O$ is assigned.

It therefore appears that there is still a difference of opinion as to the existence of compounds of the type $M_2Pt(CN)_5$. Very little has appeared on this subject since the publication of Hadow's experiments in 1861, and a complete investigation of the subject is therefore desirable. In addition to this, presuming the non-existence of the compounds $M_2Pt(CN)_5$, the preparation of a series of true platinicyanides, that is, salts which bear a relationship to the platinocyanides similar to that existing between ferri- and ferrocyanides, would be of considerable interest.

EXPERIMENTAL.

Owing to the very high molecular weight of the compounds under examination, their analysis is a matter of some difficulty. One molecule of halogen, etc., is frequently found in these compounds in combination with several molecules of a platinocyanide; hence the determination of the percentage composition does not afford a sufficiently accurate guide to the actual composition of the substance.

Several special methods of examination were employed; by their aid a greater insight into the actual constitution of the compounds was arrived at.

The following methods were employed:

(*a*) The oxidising power, or percentage of electronegative group combined with the platinocyanide molecule, was estimated by the determination of the amount of iodine liberated from a solution of potassium iodine. In the majority of cases the substances are by no means fully halogenated, and the proportion between the completely oxidised platinocyanide and the unchanged salt, with which it is combined, was determined by the complete bromination of the substance and the estimation of the iodine liberated from potassium iodine by the completely oxidised substance.

The accuracy of this method of analysis requires checking, as there is apparently a tendency on the part of the perbromoplatinocyanide to part with a little bromine on prolonged boiling. In addition to this it is often very difficult to remove the last traces of a dissolved gas from its aqueous solution, and it is therefore necessary to ascertain the duration of boiling which is requisite for the complete removal of the free bromine.

A solution of pure crystallised barium platinocyanide,

$$BaPt(CN)_4,4H_2O,$$

was treated with excess of bromine, and the solution boiled for ten minutes after the apparent disappearance of all the free bromine:

0·3382 liberated 0·1702 iodine.

$BaPt(CN)_4,4H_2O$ requires 0·1707.

A few drops of bromine were added to 50 c.c. of water; the mixture after boiling for ten minutes did not liberate any iodine from potassium iodide, thus proving that no bromine is retained.

(*b*) The majority of the oxidation products under examination consist of a molecule of completely oxidised platinocyanide combined with several molecules of the unaltered salt. The oxidised compounds, in all those cases examined, do not yield any precipitate with zinc sulphate, whereas in the case of platinocyanides the zinc salt is quite insoluble. The precipitation of zinc platinocyanide thus enables an estimation of the proportion of platinocyanide to oxidised compound to be ascertained. This ratio is obtained by the precipitation of zinc platinocyanide, both from the compound itself and after its reduction by sulphur dioxide. The value so obtained affords a check on that arrived at by the iodine method.

The accuracy of this estimation was proved by the precipitation of zinc platinocyanide from the potassium salt derived from a known quantity of the pure crystallised barium compound. The latter is very readily obtained in a pure state, and is more convenient than the potassium salt, which is not so easily prepared in a state of purity:

0·6029 of barium platinocyanide, after conversion into the potassium salt, gave 0·4261 $ZnPt(CN)_4$. $ZnPt(CN)_4 = 70·7$ per cent. of the weight of barium salt.

$BaPt(CN)_4,4H_2O$ requires $ZnPt(CN)_4 = 71·3$ per cent.

(*c*) The basic metal and platinum were estimated by ignition with pure concentrated sulphuric acid in a porcelain crucible. The basic metal is converted into sulphate, which remains mixed with metallic platinum. It is desirable to make this estimation on a sample of the salt which has been previously employed for the determination of the water of crystallisation. If the hydrated compound is used, on heating with sulphuric acid the mixture creeps up the sides of the crucible, rendering this analysis liable to error.

(*d*) The cyanogen group was estimated by the determination of the nitrogen by Dumas' method. A considerable degree of heat is necessary in order to effect the complete decomposition of the very stable platinocyanide grouping. A few determinations were made by oxidation with chromic and sulphuric acids, the cyanogen groups being oxidised to carbon dioxide. The values obtained by this method were not so satisfactory.

Action of Bromine on Potassium Platinocyanide.

The bromine compound is preferable to that obtained by the action of chlorine for the investigation of the action of the halogens on potassium platinocyanide, owing to the fact that the higher atomic weight of bromine makes the percentage of halogen in the molecule much greater. It has the additional advantage of facility of preparation. The compound was prepared by completely brominating a sixth portion of a saturated solution of potassium platinocyanide, and, after the excess of bromine was removed by boiling, adding the remaining five-sixths. The liquid so obtained was allowed to crystallise slowly in a desiccator. The first crystals deposited were collected, and drained as completely as possible by the aid of the pump. The product, after washing in a little water and drying in a desiccator, was obtained in well-developed needle-shaped crystals about half an inch long, which have the appearance of metallic copper. The crystals are readily soluble in cold water, yielding a pale yellow solution. When heated with sulphuric acid and a little manganese dioxide, bromine is evolved, thus proving the presence of this element. The salt has strong oxidising properties, and causes the immediate liberation of iodine from potassium iodide.

All the water of crystallisation is expelled at 120°; the colour changes to dark bluish-green, whilst the crystalline form remains unaltered. On exposure of the anhydrous compound to the atmosphere, water is absorbed, and the salt regains its coppery appearance. On heating to a little above 200°, cyanogen is evolved, platinous cyanide is formed, and the bromine remains as potassium bromide. The salt therefore gives a turbid solution after heating, owing to the presence of yellowish-green, insoluble platinous cyanide.

The behaviour of the compound is in many respects like that of a solution of free bromine, but no evolution of this element could be detected by drawing air through the solution for a long time:

1·0254 liberated 0·0844 iodine, corresponding with 0·0528 bromine. Br = 5·15. 0·8487, after complete bromination, liberated 0·5069 iodine.

Iodine liberated = 8·23 per cent.

Iodine liberated after complete bromination = 59·7 per cent.

These observations prove that the completely brominated compound liberates seven times the quantity of iodine set free by the compound itself. The proportion of platinocyanide to perbromoplatinocyanide is therefore 6 to 1.

This ratio was confirmed by the precipitation of zinc platinocyanide:

0·4704 gave 0·3205 $ZnPt(CN)_4$ = 70 per cent. of the weight of the salt.

$[K_2Pt(CN)_4]_6,K_2Pt(CN)_4Br_2,16H_2O$ requires $ZnPt(CN)_4=70\cdot7$ per cent.

$[K_2Pt(CN)_4]_5,K_2Pt(CN)_4Br_2,18H_2O$ requires $ZnPt(CN)_4=65\cdot5$ per cent.

The determination of the percentage composition scarcely serves to settle the ratio owing to the very high molecular weight of the compound.

The following results were obtained. Owing to the fact that the needles have a tendency to lose water, the results of the analysis are calculated for the anhydrous salt, the values for the compounds containing five and six molecules of platinocyanide to one of perbromoplatinocyanide being calculated similarly:

0·2019 gave 0·0921 Pt and 0·0777 K_2SO_4. Pt = 45·6; K = 17·2.
0·1760 „ 20·3 c.c. N_2 at 17° and 745·5 mm. CN = 24·3.

Found: K = 19; Pt = 50; CN = 26·6; Br = 5·7.

$[K_2Pt(CN)_4]_6,K_2Pt(CN)_4Br_2$ requires K = 19·6; Pt = 48·8; CN = 26; Br = 5·7 per cent.

$[K_2Pt(CN)_4]_5,K_2Pt(CN)_4Br_2$ requires K = 19·3; Pt = 48·3; CN = 25·7; Br = 6·6 per cent.

The sample of salt analysed contained 9 per cent. of water. This corresponds with 16 molecules of water.

Hadow obtained the value 5 : 1 for the ratio of platinocyanide to perhalogenated salt. This ratio was arrived at by the complete oxidation of potassium platinocyanide, and of the intermediate product by permanganate in the presence of hydrochloric acid. Attempts were made by the author to obtain a value for the ratio by this method, manganese sulphate being added to prevent the oxidation of the hydrochloric acid. The end-points were very indeterminate, whereas the iodine method is very accurate and trustworthy. Hadow's analysis of the percentage of chlorine gave values corresponding with between 6 and 7 atoms of platinum to 1 molecule of chlorine.

Precipitation of the silver salt by means of standard silver nitrate solution affords a further confirmation of the 6 : 1 ratio. An orange-yellow precipitate is immediately formed, which consists of a solid solution of silver platinocyanide and perbromoplatinocyanide. There was no evidence of any separate fractional precipitation of silver bromide or of silver perbromoplatinocyanide:

0·3362 requires 15 c.c. $N/10$-$AgNO_3$ for complete precipitation; hence 1 gram requires 44·6 c.c.

$[K_2Pt(CN)_4]_6,K_2Pt(CN)_4Br_2,16H_2O$ requires 44·8 c.c.
$[K_2Pt(CN)_4]_5,K_2Pt(CN)_4Br_2,18H_2O$ „ 43·7 „

It is stated in Watts' "Dictionary of Chemistry," Vol. II., p. 345, that silver nitrate causes the precipitation of a mixture of silver bromide and platinocyanide, but this is not so, since such a mixture would be practically colourless. Further proof was afforded by completely brominating the salt, and precipitating it by silver nitrate:

0·2916 required 13·2 c.c. $N/10$-$AgNO_3$. 1 gram requires 45·2 c.c., that is, the same amount as is required by the salt when not treated with bromine. It is hardly to be expected that the addition of silver nitrate would determine the precipitation of silver bromide, seeing that the bromine is not ionic.

Platinocyanides may form more than one double compound with the perhalogen salts. Various proportions of equivalent strength solutions of potassium platinocyanide and perbromoplatinocyanide were therefore mixed together, and allowed to evaporate to dryness. The crystallised residue was examined under a microscope:

$K_2Pt(CN)_4Br_2$.	$K_2Pt(CN)_4$.	Result.
1	1	Coppery needles mixed with yellow perbromo-salt
1	3	,, ,, ,, ,, ,,
1	4	,, ,, ,, ,, ,,
1	5	,, ,, only visible
1	6	,, ,, ,,
1	7	,, ,, with potassium platinocyanide

The results are not very conclusive, but they serve to indicate that the two salts combine together in one proportion only, and that this is either 5 : 1 or 6 : 1.

The same crystals are obtained from a mixture of the two salts, whether the crystallisation is allowed to take place at 0° or 100°. This proves that the transition point does not lie within this range.

The experiments described clearly prove that the ratio of platinocyanide to perbromoplatinocyanide is 6 : 1, and not 5 : 1 as stated by Hadow. The three different methods employed for the determination of this ratio all lead to this conclusion. No evidence was obtained of the formation of any other compound, for example, $K_2Pt(CN)_5$, by the action of bromine on potassium platinocyanide.

Action of Peroxides on Platinocyanides.

(1) *Action of Lead Peroxide.*—The observation that a solution of potassium platinocyanide, acidulated with sulphuric acid, yields a product containing the SO_4 group, was made by Hadow (*Quart. Journ. Chem. Soc.*, 1861, **14**, 106), but no analyses of the product were published.

Lead peroxide was slowly dropped into a concentrated solution of potassium platinocyanide acidulated with a little dilute sulphuric acid. Each particle of peroxide on entering the liquid was instantly surrounded by a growth of minute, bronze-coloured needles

The solution was warmed in order to dissolve the crystals, the excess of peroxide collected, and the clear filtrate allowed to crystallise. The mother liquor was drained off the crystals, which were washed with a little cold water. The salt is thus obtained in very minute, bronze-coloured, needle-shaped crystals. These liberate iodine from potassium iodide, and are readily soluble in cold water; but the solution displays a great tendency to decompose with the separation of platinous cyanide. For this reason the determination of the ratio of SO_4 to Pt cannot be made with great accuracy, and the value obtained by the estimation of the iodine liberated from potassium iodide, before and after oxidation by bromine, is questionable. Owing to the high molecular weight of the compound, the difference in the percentage composition for various ratios is very small:

0·3298 liberated 0·0218 of iodine.

0·2473, after boiling with bromine, liberated 0·1523 of iodine.

These observations give the ratio of platinocyanide to oxidised compound as 9:1:

0·4640 gave 0·0269 $BaSO_4$. $SO_4 = 2·4$.
0·4732 „ 0·0314 H_2O. $H_2O = 6·6$.
0·4732 „ 0·1873 K_2SO_4 and 0·2196 Pt. K = 17·7; Pt = 46·4.

The compound has the composition $xK_2Pt(CN)_4,yK_2Pt(CN)_4SO_4$, where $x:y$ is probably 9:1. This value cannot, however, be definitely accepted owing to the difficulties of accurate analysis already mentioned.

The salt behaves like the sulphate of a feebly electronegative metal. It undergoes double decomposition with barium salts, and by treatment with the calculated quantities of barium cyanide and platinocyanide, bronze needles are obtained, which are of interest as representing an oxidised condition of a platinocyanide due to the addition to the molecule of the groups CN and $Pt(CN)_4$.

(2) *Action of Manganese Dioxide.*—The following analyses prove that the same compound is obtained if manganese dioxide is employed in place of lead peroxide. The results are slightly vitiated by traces of manganese sulphate, which make the potassium too high and interfere with the complete bromination figure:

0·3347 liberated 0·2180 iodine. 0·2286, after complete bromination, liberated 0 1520 iodine; hence the ratio of platinocyanide to oxidised salt is 9:1:

0·3278 gave 0·1400 K_2SO_4 and 0·1527 Pt.

	Calculated for the anhydrous compounds.		
	Product of action of PbO_2.	Product of action of MnO_2.	Calculated.
K	19·0	20·4	20·1
Pt	50·0	50·2	50·2
SO_4 (by iodine) ...	2·6	2·6	2·8
SO_4 (by $BaSO_4$) ...	—	—	—

(3) *Action of Hydrogen Peroxide.*—As the separation of the sulphoplatinocyanide, obtained by the action of lead peroxide, is somewhat troublesome, hydrogen peroxide was employed instead, in order to prepare the same compound more readily. Contrary to expectation, a totally different compound is produced.

If white, fluorescent crystals of potassium platinocyanide are boiled with hydrogen peroxide (20 volume), the crystals remaining after evaporation are pale yellowish-green and non-fluorescent. They consist of an isomeric non-fluorescent modification of potassium platinocyanide (see Trans., 1908, **93**, 1446), into which the white, fluorescent variety has been transformed by the catalytic action of some (probably acid) impurity in the peroxide. This is proved to be the case by boiling the white, fluorescent crystals with "perhydrol," which leaves them quite unaffected.

Following up former experiments, hydrogen peroxide and sulphuric acid were employed instead of lead or manganese dioxides for the oxidation of potassium platinocyanide. On the addition of hydrogen peroxide (20 volume) to a concentrated solution of potassium platinocyanide acidulated with sulphuric acid, bronze, needle-shaped crystals displaying a strong metallic reflexion are deposited if the concentration of the solution is sufficient. After evaporation over a water-bath, the solution deposits a considerable quantity of the compound on cooling. The crystals are purified by draining off the mother liquor and washing with a little cold water. When dried they display a fine bronze colour, quite different from the darker and more coppery hue of the product of the action of lead peroxide. The salt is readily soluble in water, yielding a colourless solution, from which no precipitate is obtained on the addition of barium chloride. If the salt is strongly heated and the residue dissolved in water, the solution after filtration likewise gives no precipitate with barium chloride. These observations prove the absence of the SO_4-group, either in the ionic condition or as part of a complex ion. The compound has strong oxidising properties, and readily liberates iodine from potassium iodide, bleaches cochineal, etc. It loses its water of crystallisation on heating to 120°, but remains otherwise unaltered, as its oxidising power is the same as that of the original substance. On heating to 200° the oxidising power is destroyed, and the residue, when dissolved in water, forms a cloudy solution owing to the presence of yellowish-green, platinous cyanide. This solution contains potassium platinocyanide and potassium cyanide. The addition of potassium cyanide re-converts the salt into potassium platinocyanide. Much decomposition into platinous cyanide is caused by boiling with hydrochloric acid; a spongy, coppery product remains on filtering and evaporation of the filtrate:

0·5490 gave 0·2100 K_2SO_4 and 0·2700 Pt. K = 17·1; Pt = 49·2.
0·1865 „ 20·9 c.c. N_2 at 13° and 754·5 mm. CN = 24·9.
0·3801 „ 0·0265 H_2O. H_2O = 6·9.

These results prove that the ratio of platinum to cyanogen is the same as in platinocyanides, but that the ratio of potassium to platinum is less than in these salts. Four atoms of platinum are associated with seven atoms of potassium instead of with eight, as in the case of platinocyanides; hence one potassium atom has been removed by the oxidation:

0·5148 liberated 0·0442 iodine. This observation corresponds with the liberation of one atom of iodine for every four atoms of platinum.

0·2127, after boiling with bromine, liberated 0·1459 iodine, that is, eight times the amount of iodine liberated by the compound itself.

The formula of the compound calculated from the percentage composition is $K_7Pt_4(CN)_{16},6H_2O$, which may be written as

$$3K_2Pt(CN)_4,KPt(CN)_4,6H_2O.$$

The three molecules of potassium platinocyanide are converted into $K_2Pt(CN)_4Br_2$ on boiling with bromine; the remainder, $KPt(CN)_4$, is rapidly converted into a platinocyanide, probably $KHPt(CN)_4$, which then combines with two atoms of bromine. The iodine liberated by the compound after treatment with bromine is thus eight times the amount liberated by the compound itself.

The reaction with potassium iodide is as follows:

$$3K_2Pt(CN)_4,KPt(CN)_4 + KI = 4K_2Pt(CN)_4 + I.$$

This composition receives additional support from the results obtained by the precipitation of the silver salt. Silver nitrate gives a light yellow, flocculent precipitate:

0·2102 required 9·5 c.c. $N/10$-$AgNO_3$. Calculated amount for the above formula = 9·3 c.c.

The addition of zinc sulphate to a cold solution does not yield an immediate precipitate, the formation of zinc platinocyanide taking place in a minute or two. After the zinc platinocyanide has been deposited, the solution is found to have lost most of its oxidising power, indicating that the residue, $KPt(CN)_4$, is rapidly decomposed in aqueous solution. (It is shown below that the zinc salt corresponding with $KPt(CN)_4$ is soluble.)

0·3126 gave 0·2139 $ZnPt(CN)_4$, corresponding with 68·4 per cent. of the weight of salt.

If $3K_2Pt(CN)_4$ is precipitated, the weight of zinc platinocyanide would be 66 per cent. The slight excess observed is due to the incipient decomposition of the compound $KPt(CN)_4$ after the protecting influence of the platinocyanide molecules combined therewith has been removed by their precipitation.

Found: K = 17·1; Pt = 49·2; CN = 24·9; H_2O = 6·9. Calc., K = 17·3; Pt = 49·6; CN = 26·4; H_2O = 6·8 per cent.

This compound may be regarded as a molecular combination of a platinocyanide with the platinicyanide, $KPt(CN)_4$, which can be written $KCN,Pt(CN)_3$. As the latter has such a great tendency to combine with the unoxidised platinocyanide, the process of oxidation was reversed by the slow addition of a concentrated solution of potassium platinocyanide to a mixture of hydrogen peroxide with a little sulphuric acid, in order that the salt $KPt(CN)_4$ only might be obtained. This, however, was not achieved, as the same product resulted.

On passing carbon dioxide into a mixture of concentrated potassium platinocyanide solution and hydrogen peroxide, the same product is obtained. This indicates that it is only necessary to maintain the solution slightly acid in order that the oxidation may proceed.

Sodium peroxide, when added to a mixture of potassium platinocyanide and dilute sulphuric acid, yields the same substance provided that the quantity of acid is sufficient to prevent the solution becoming alkaline.

After the completion of these experiments it was found that Willm (*Ber.*, 1888, **21**, 1434) had prepared the same compound. The observations detailed above are mostly different from his, and are more complete. They are given in full, as they have a considerable bearing on what follows.

Oxidation of Lithium Platinocyanide.

The oxidation of lithium platinocyanide by hydrogen peroxide in the presence of sulphuric acid yields a similar product, but its constitution is not identical with that of the potassium compound. A solution of lithium platinocyanide was mixed with a little dilute sulphuric acid, a few c.c. of hydrogen peroxide (20 volume) were added, and the mixture was carefully evaporated over a water-bath. A copper-coloured salt, which is considerably redder than the potassium compound, was obtained:

0·2105 gave 0·0865 Pt. Pt = 41.

0·2414 required 8·5 c.c. $N/10\text{-}AgNO_3$. Li = 2·4.

0·4177 liberated 0·0384 iodine; hence one atom of iodine is liberated for every three atoms of platinum.

0·2960, after boiling with bromine, liberated 0·1677 iodine, that is, six times the amount liberated by the compound itself.

The lithium was estimated by the precipitation of the silver salt, as it is very difficult to free the compound from traces of lithium sulphate.

These analyses prove that five atoms of lithium are associated with three of platinum, and that the constitution of the anhydrous compound is $2Li_2Pt(CN)_4,LiPt(CN)_4$.

Found: Li = 11·4; Pt = 195; I liberated = 43·6. Calc. (for 1 atom of platinum), Li = 11·7; Pt = 195; I liberated = 42·6.

The tendency of the two salts to combine together is not so great as in the case of the potassium compound (see later), which may account for the fact that only two molecules of platinocyanide are associated with every molecule of platinicyanide.

Oxidation of Sodium Platinocyanide.

A moderately concentrated solution of sodium platinocyanide, acidulated with a little dilute sulphuric acid, was treated with a small quantity of hydrogen peroxide (20 volume), and very carefully evaporated over a water-bath. A coppery-red, crystalline residue remained:

0·3344 gave 0·1259 Pt. Pt = 37·7.

0·3830 required 12·15 c.c. $N/10$-$AgNO_3$. Na = 7·3.

0·4410 liberated 0·0352 iodine; hence 1 atom of iodine is liberated for every three atoms of platinum. The constitution of the anhydrous compound is therefore $2Na_2Pt(CN)_4,NaPt(CN)_4$.

Found: Na = 38; Pt = 195; I liberated = 41·9. Calc. (for 1 atom of Pt), Na = 38·3; Pt = 195; I liberated = 42·6.

The oxidation product is therefore similar to that resulting from the oxidation of lithium platinocyanide, the ratio of platinocyanide to platinicyanide being 2:1.

Action of Hydrogen Peroxide on Hydroplatinocyanic Acid.

Hydrogen peroxide does not oxidise platinocyanides in neutral or alkaline solution, as the solution must be maintained in a slightly acidulated condition in order that the oxidation may be effected. Treatment of hydroplatinocyanic acid with hydrogen peroxide avoids the necessity of acidulation by a third substance; it is also possible that hydroplatinocyanic acid may not display any great tendency towards combination with its oxidation product.

Hydrogen peroxide (20 volume) was added to a fairly concentrated solution of hydroplatinocyanic acid, the mixture afterwards being carefully evaporated over a water-bath. A white substance of a somewhat viscid nature was first produced. On further evaporation this became in turn pink, brown, and finally dull olive-green. A portion of the same mixture was evaporated in a desiccator over sulphuric acid. A transparent, colourless jelly remained, which gradually turned pink, then brown, at the same time losing its jelly-like consistency. Desiccation under atmospheric pressure over sulphuric acid does not yield the green product. The brown and olive-green substances dissolve in water after preliminary re-hydration; that is, the green product turns brown and then white before it passes into solution. The white, brown, and green substances are all of the same composition, and differ merely in their content of water.

The green product leaves a light yellow residue on heating to 120°. This is insoluble in water, but dissolves in a boiling solution of potassium cyanide, the resulting liquid being devoid of oxidising properties:

0·3598 gave 0·2638 Pt. Pt = 73·3.

$Pt(CN)_2$ requires Pt = 78·9 per cent.
$Pt(CN)_3$ „ Pt = 71·4 „ „

The residue on heating therefore approximates in composition to platinum tricyanide, $Pt(CN)_3$.

The aqueous solution of the olive-green substance has the following properties, which are tabulated beside those of hydroplatinocyanic acid for purposes of comparison.

Reagent added to	(*a*) green product.	(*b*) $H_2Pt(CN)_4$.
KI	Iodine is at once liberated, but the reaction is not instantaneous. The rate of liberation rapidly decreases and the reaction is practically completed in four hours.	No liberation of iodine.
$CuCl_2$	No precipitate, unless the solution is concentrated, in which case a dull green, granular precipitate is deposited.	Bluish-green, flocculen precipitate, even from very dilute solutions.
$ZnSO_4$	No precipitate.	White, granular precipitate.
$AgNO_3$	Light brown, flocculent precipitate which rapidly settles.	White precipitate.
SO_2............	When boiled with sulphurous acid, the solution is reduced with the regeneration of platinocyanide.	No action.
$K_2Pt(CN)_4$...	When concentrated solutions of the green product and potassium platinocyanide are mixed, bronze needles, exactly similar in appearance to those resulting from the action of hydrogen peroxide and sulphuric acid on potassium platinocyanide, are produced.	No action.

The solution has an acid reaction:

0·3770 gave 0·2168 Pt. Pt = 58.
0·2250 „ 29·5 c.c. N_2 at 17° and 750·5 mm. CN = 28.
0·5600 „ 0·0559 H_2O. H_2O = 10.
0·7484 liberated 0·2790 iodine.

These results show that the ratio of CN groups to atoms of platinum is 4 : 1, the same as in platinocyanides. One atom of iodine is liberated for every atom of platinum.

The aqueous solution was titrated with *N*/10-sodium hydroxide, phenolphthalein, methyl-orange, and litmus being all employed as indicators, but the values obtained are not at all trustworthy, owing to the fact that all these substances are rapidly bleached:

0·5274 required approximately 21 c.c. *N*/10-sodium hydroxide.

Methyl orange was used as an indicator, and was added when the solution was nearly neutral. This observation gives 5 : 4 as the ratio of hydrogen to platinum. The exact value of this ratio was finally determined by precipitation of the silver salt with *N*/10-silver nitrate:

0·4652 required 15·4 c.c. *N*/10-$AgNO_3$.

This observation gives practically 1 : 1 as the ratio of silver (or hydrogen) to platinum. It was observed that the flocculent, brown precipitate of the silver salt was first obtained, but that just at the finish of the precipitation a very small amount of a white precipitate of silver platinocyanide was formed. (Silver platinocyanide is most readily identified by boiling with barium chloride, the well known and easily recognised barium salt being produced.) The substance therefore contains a small proportion of unchanged platinocyanide. This affords an explanation of the slight excess above 1 : 1 of the ratio of silver to platinum, and also of the slight variation from 1 in the opposite direction for the ratio of iodine liberated to platinum.

The exact figures are:

	Difference.
Ratio of iodine to platinum 0·98	−0·2
Ratio of silver to platinum 1·1	+0·1

0·5273 gave 0·6563 of silver salt. Calculated value = 0·644.

Here, again, a slight excess above the calculated value is due to the precipitation of a small quantity of silver platinocyanide.

The compound is stable in aqueous solution, as the same amount of silver nitrate is required for its precipitation after the solution has been made for a week.

The oxidising properties of the compound are not due to combined hydrogen peroxide. This was proved by leaving a portion of the solution in contact with platinum-black for a week, and then estimating the iodine liberated from potassium iodide. A solution of 0·3759, after a week's contact with platinum-black, liberated 0·1446 iodine; therefore, 38·4 grams of iodine were liberated per cent. of salt used, and 37·3 grams of iodine were liberated per cent. of salt used immediately after solution.

The above observations prove that:

(1) The ratio of hydrogen to platinum is 1:1.

(2) The ratio of CN to platinum is 4:1.

The simplest formula for the compound is therefore

$$HPt(CN)_4,xH_2O,$$

and for the silver salt, $AgPt(CN)_4$.

The green product contains 10 per cent. of water, which corresponds approximately with two molecules of water.

Found: $Pt = 58$; $CN = 28$; $H_2O = 10$.

$HPt(CN)_4,2H_2O$ requires $Pt = 58$; $CN = 30·9$; $H_2O = 10·7$ per cent.

The oxidation reaction is very simple:

$$H_2O_2 + 2H_2Pt(CN)_4 = 2H_2O + 2HPt(CN)_4.$$

The reaction with potassium iodide is:

$$KI + HPt(CN)_4 = KHPt(CN)_4 + I.$$

Thus one atom of iodine is liberated for each atom of platinum.

The salts $HPt(CN)_4$ and $AgPt(CN)_4$ are true platinicyanides, bearing a relationship to the platinocyanides similar to that existing between ferri- and ferro-cyanides. They can be regarded as compounds of cyanides with the hitherto unknown platinum tricyanide, $Pt(CN)_3$. The substance which remains on heating hydroplatinicyanic acid to 120° has a composition which approximates to $Pt(CN)_3$.

The brown, flocculent precipitate, obtained on adding silver nitrate to a solution of hydroplatinicyanic acid, dries to a dark buff powder. This leaves a residue of silver and platinum on gentle ignition:

0·4636 lost 0·1172. $CN = 25·3$.

0·4636 gave 0·2137 Pt and 0·1725 AgCl. $Pt = 46·1$; $Ag = 27·9$.

$AgPt(CN)_4$ requires $Ag = 26·5$; $Pt = 47·9$; $CN = 25·5$ per cent.

Silver platinocyanide, when precipitated from neutral solutions, is a white, flocculent precipitate; silver platinicyanide is brown and flocculent. The precipitate resulting from the intermediate potassium platinoplatinicyanide is pale yellow and flocculent, and from the lithium salt deeper yellow. These are solid solutions of silver platinocyanide and platinicyanide, in which the former predominates. No separate precipitation of platinicyanide and platinocyanide was observed, as is the case when hydroplatinicyanic acid, containing a trace of platinocyanide, is treated with silver nitrate. Silver platinicyanide is soluble in ammonia, and is reprecipitated by the addition of nitric acid.

Action of "Perhydrol" on Platinocyanides.

It has been shown that the oxidising power of hydrogen peroxide (20 volume) is insufficiently potent to destroy the union between the platino- and platini-cyanides of potassium and lithium, although it is able to effect the complete oxidation of hydroplatinocyanic acid. The action of "perhydrol" was therefore investigated in order to ascertain if this more concentrated preparation of hydrogen peroxide was capable of completely oxidising the salts which resist the action of the weaker solution.

Action on Potassium Platinocyanide.—Crystals of potassium platinocyanide were treated with a few c.c. of "perhydrol" and a little dilute sulphuric acid. The mixture was heated on a water-bath, and after evaporation a dark blue product remained. This turns white on moistening with water, and readily passes into solution:

0·3272 gave 0·1208 Pt. Pt = 37.

0·5235 liberated 0·0932 iodine.

This corresponds with the liberation of nearly 1 atom of iodine for each atom of platinum present:

0·6868 required 16 c.c. $N/10$-$AgNO_3$.

K = 9; hence 47 parts of potassium are combined with 195 of platinum.

Silver nitrate gives a light brown precipitate of the salt $AgPt(CN)_4$. These results show that the product is potassium platinicyanide, $KPt(CN)_4$ (mixed with a small quantity of unchanged double salt), and that the combination between the platinocyanide and platinicyanide is destroyed by oxidation with "perhydrol." The same product is obtained if the bronze intermediate compound is employed instead of potassium platinocyanide.

Action on Lithium Platinocyanide.—The reaction with lithium platinocyanide and with the intermediate compound is similar. Both salts are completely oxidised to platinicyanide.

Lithium platinicyanide is colourless, but dehydration causes it to become successively yellow and brownish-red. It can be prepared by allowing a solution of lithium platinocyanide mixed with "perhydrol" and a little sulphuric acid to evaporate in a desiccator. Lithium platinocyanide is more readily oxidised than the potassium salt, as the complete oxidation can be effected in solutions considerably more dilute than is possible in the case of potassium platinocyanide. The complete oxidation can even be effected by hydrogen peroxide (20 volume) if the solution of lithium platinocyanide is very concentrated:

0·3905 gave 0·1324 Pt. Pt = 34.

0·3830 liberated 0·0896 iodine, corresponding with one atom of iodine for every atom of platinum.

0·2836 required 5·7 c.c. $N/10$-$AgNO_3$. Li = 1·4.

Silver nitrate gives a light brown precipitate of silver platinicyanide. These observations prove that the product of the oxidation is represented by the formula $LiPt(CN)_4$.

Found: Li = 8; Pt = 195; I liberated = 134. Calc. (for 1 atom of Pt), Li = 7; Pt = 195; I liberated = 128.

It will be noticed that the oxidation is practically complete, and that there is no unchanged platinocyanide or double salt. The compound immediately forms coppery needles with lithium or potassium platinocyanide.

Action on Sodium Platinocyanide.—The reaction is the same as in the case of lithium platinocyanide. On treatment of a fairly concentrated solution of sodium platinocyanide acidulated with sulphuric acid with "perhydrol," sodium platinicyanide is obtained. This salt forms purple, needle-shaped crystals, which turn white on the addition of water before dissolving. The crystalline form of this compound was better developed than in the case of any other platinicyanides which were examined:

0·2847 gave 0·1081 Pt. Pt = 38.

0·3143 required 6·7 c.c. $N/10$-$AgNO_3$. Na = 4·9.

0·3580 liberated 0·0864 iodine.

As in the case of the lithium salt, it is possible to oxidise sodium platinocyanide to the platinicyanide by hydrogen peroxide (20 volume) if the solutions are very concentrated.

Found: Na = 25; Pt = 195; I liberated = 124. Calc. (for 1 atom Pt), Na = 23; Pt = 195; I liberated = 128.

Action on Rubidium Platinocyanide.—Rubidium platinocyanide appears to be rather more difficult to oxidise completely than the lithium and sodium salts. Crystals of this compound were mixed with the calculated amount of sulphuric acid, and treated with a few c.c. of "perhydrol." The mixture was evaporated over a water-bath, and a coppery-red product was obtained, which yielded the following results on analysis:

0·2290 gave 0·0753 Pt. Pt = 32·9.

0·3016 required 7·9 c.c. $N/10$-$AgNO_3$. Rb = 22·2.

0·2872 liberated 0·0230 I. I liberated = 8.

These results show that the composition of the red crystals is approximately $RbPt(CN)_4,2Rb_2Pt(CN)_4,xH_2O$ (the proportion of $RbPt(CN)_4$ is rather greater than this).

If the red crystals are treated with more "perhydrol," a white residue of $RbPt(CN)_4$ is obtained. The white compound readily forms coppery needles with potassium platinocyanide solution, and gives a buff precipitate with silver nitrate. On dehydration it turns pink. It is very similar in appearance to the lithium and hydrogen salts.

The salts of the alkali metals cannot exist in alkaline solutions. Even in neutral solution the compounds are rapidly reconverted into platinocyanides. The speedy loss of oxidising power experienced by the solution of the intermediate compounds on the precipitation of the platinocyanide molecules by zinc sulphate is explained by this fact.

Conclusions.

(1) Two products only result from the action of bromine on potassium platinocyanide: the perbromo-compound, $K_2Pt(CN)_4Br_2$, and a compound of this substance with unchanged platinocyanide. Hadow's explanation of the action of chlorine and bromine is correct, but the formula assigned by him to the intermediate compound is not quite accurate. The constitution of this salt is found to be $6K_2Pt(CN)_4,K_2Pt(CN)_4Br_2$. This composition is in agreement with Werner's theories for the structure of a platino-compound associated with one molecule of a platini-salt. There is no evidence of the formation of any other compound such as $K_2Pt(CN)_5$, the true platinicyanides having a different composition (see below). If the compound $M_2Pt(CN)_5$ were obtained by the oxidation of a platinocyanide, platinum should be separated from the complex anion. This is contrary to the great stability of the platinocyanides, and no indications of such a separation were ever obtained.

It appears from consideration of the properties of the platinum ammonia compounds $PtX_4(NH_3)_2$ (where X = halogen atom) that halogen atoms directly united to platinum do not form ions on solution. Hence, the bromine in perbromoplatinocyanides is directly united to the platinum. According to Werner's hypothesis, its constitution is represented by:

$$M_2\left[Pt\begin{matrix}(CN)_4\\(Br)_2\end{matrix}\right],$$

and it should exist in two modifications. No differences, however, could be detected between preparations of this compound which were derived from the yellow and green varieties of barium platinocyanides.

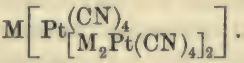
The union between the halogen and platinum is fairly strong, as no evolution of bromine could be detected on drawing air through a solution of the salt, and treatment with carbon disulphide failed to extract any halogen. The mode of attachment is, however, quite different in character to that of the CN-groups, as the action of alkalis so very readily regenerates a platinocyanide.

(2) Peroxides, having the structure O:X:O, in which doubly-linked oxygen atoms are attached to the central atom, oxidise potassium platinocyanide in the presence of dilute sulphuric acid, giving a compound of similar type to the haloid intermediate products, in which two halogen atoms are replaced by the group SO_4. The salt has the composition:

$$9K_2Pt(CN)_4,K_2Pt(CN)_4,K_2Pt(CN)_4SO_4,xH_2O.$$

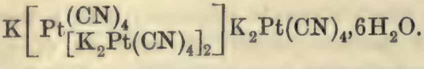
It behaves like the sulphate of a feebly electropositive metal, and enters into double decomposition with barium salts. The SO_4-group is replaced by the acid radicle attached to the barium.

(3) Hydrogen peroxide has a totally different action. (Other peroxides behave similarly to hydrogen peroxide, but in all probability they act by first yielding hydrogen peroxide, to which the oxidation is really due.) Platinocyanides of the alkali metals are oxidised in the presence of a little dilute sulphuric acid, the group $Pt^{II}(CN)_4$ becoming $Pt^{I}(CN)_4$, corresponding with the compound $MPt(CN)_4$. Adopting Werner's views, we can represent these compounds by the following formula:



$$M\left[Pt\begin{matrix}(CN)_4\\ [M_2Pt(CN)_4]_2\end{matrix}\right].$$

They are characterised by a coppery or bronze lustre, and are very similar in appearance to the intermediate halogen additive products. As no portion of the sulphuric acid enters the molecule of the oxidised product, its function is merely to maintain the acidity of the solution. This is proved to be the case, as the oxidation may be effected, even in the presence of carbonic acid. It is a remarkable fact that the product resulting from the oxidation of potassium platinocyanide contains one more molecule of platinocyanide associated with the platinicyanide. It can be represented in the following way:



$$K\left[Pt\begin{matrix}(CN)_4\\ [K_2Pt(CN)_4]_2\end{matrix}\right]K_2Pt(CN)_4,6H_2O.$$

The properties of this compound, as might be expected, differ somewhat from the salts which are obtained by the oxidation of the platinocyanides of the other alkali metals, inasmuch as it is far more difficult to oxidise to the platinicyanide, $KPt(CN)_4$.

In the case of hydroplatinocyanic acid, oxidation with hydrogen peroxide (20 volume) yields the compound $HPt(CN)_4$, and the intermediate platinoplatinicyanide is not obtained. This salt can, however, readily be prepared synthetically; on mixing together concentrated solutions of the platino- and platini-cyanides of hydrogen, bronze needles of a double compound are produced at once.

The combination between platinocyanide and platinicyanide probably exists in solution. Evidence for this view is afforded by the precipitation by silver nitrate of a solid solution of the two silver salts (which does not occur in the case of hydroplatinicyanic acid containing a little platinocyanide), and also by the fact that the addition of zinc sulphate does not yield an immediate precipitate of zinc platinocyanide.

(4) The true platinicyanides are obtained by oxidation in the presence of dilute sulphuric acid. This reaction appears to be effected more readily with the lithium and sodium salts than in the case of the rubidium compound, but this phenomenon is in all probability a function of the relative solubilities of the oxidation products. Potassium platinocyanide, as already stated, resists complete oxidation to platinicyanide, and repeated treatments with "perhydrol" are scarcely able to effect its complete oxidation.

The platinicyanides do not usually form well-defined, crystalline substances, but the sodium salt has been prepared in the form of small, needle-shaped crystals of a deep purple colour. The acid and the salts of the alkali metals are very soluble in water. They unite immediately with platinocyanides, forming bronze-coloured, well crystallised double salts. They can be regarded as compounds of the cyanides with platinum tricyanide, $MCN,Pt(CN)_3$, platinocyanides being formulated as $2MCN,Pt(CN)_2$. The characteristic properties of the platinocyanides are not exhibited by these compounds, with the possible exception of the formation of different coloured hydrates. In this case, however, the various products are not so brightly coloured.

(5) The metallic copper or bronze-coloured lustre exhibited by the majority of the oxidation products of platinocyanides is not necessarily indicative of an oxidised condition of a portion of the compound. It appears rather to be a characteristic of the combination of several platinocyanide molecules with a nucleus which may be an oxidised platinocyanide, or may be of quite a different nature; for example, the compound $3K_2Pt(CN)_4HCl$ is obtained in the form of coppery needles indistinguishable from the haloid additive products. The author has prepared a double platinocyanide of lithium and hydrogen which simulated the appearance of metallic copper even more closely. This salt can be crystallised

out on the bottom of a glass vessel, forming a fine mesh of crystals which present to the naked eye the exact appearance of a copper mirror. Of course, neither this salt nor the hydrogen chloride compound possesses any oxidising properties.

Most of the materials required for this investigation were purchased from funds kindly furnished by the Government Grant Committee of the Royal Society, to whom the author desires to acknowledge his indebtedness.

CXIV.—*The "Crude Fat" of* Beta vulgaris.

By Allen Neville.

In the course of some work carried out in the School of Agriculture, Cambridge, large quantities of the dried root matter of the common mangel, *Beta vulgaris*, were extracted with ether and alcohol, and as the crude fat so obtained appeared not to have been previously examined, it was handed by Prof. T. B. Wood to the author for investigation.

The ethereal solution was found to contain principally fat and fatty acids, and amongst these were definitely identified palmitic, erucic, and oleic acids, the proportion between unsaturated and saturated acids being about four to one. In addition, the ethereal extract was found to contain two substances somewhat resembling the phytosterols, and to one of these melting at 155° could be assigned with considerable certainty the formula $C_{31}H_{58}O_2$. The reactions of the substance pointed to it being allied to, but not identical with, the typical phytosterols. The other substance, owing to the small quantity available, could be characterised less definitely. On analysis it gave results corresponding with the formula $C_{29}H_{45}O_2$, it melted at 120—122°, and showed no definite crystalline form, as did the first compound.

The alcoholic extract contained only a small quantity of crude fat and fatty acids, and some amorphous, flocculent material of protein nature.

EXPERIMENTAL.

Treatment of Ethereal Extract.

The matter extracted by ether amounts to only 0·1 per cent. of the mangel. The ethereal extract had been washed with dilute sodium hydroxide, and some hydrolysis may have taken place; hence perhaps the relatively large amount (61·5 per cent.) of free fatty acids obtained on acidifying and extracting the alkaline solution with ether. From the original ethereal solution 21 grams of crude fat were obtained.

The fat was hydrolysed and the 15 grams of fatty acids obtained, together with those from the original mixture, were converted into lead salts, and the saturated and unsaturated acids then separated by ether extraction. The portion soluble in ether (36 grams) is described below as Fraction *A*, whilst the insoluble portion (10·5 grams) is described as Fraction *B*.

Examination of Fraction A.—The material gave an iodine number of 80·5, thus indicating that no large proportion of the material was acids of a greater degree of unsaturation than those of the oleic series.

The substance was treated with 85 per cent. alcohol, when it was noticed that a white, flocculent material remained insoluble. This was collected (Substance *a*). To the alcoholic solution was added a slight excess of sodium ethoxide and much ether. The precipitate was collected and washed well with ether, and the ethereal solution was well washed with water. The mixed ethereal solutions were dried, and on distilling off the ether a small quantity of a white, flocculent material (Substance *b*) was obtained. The soap was decomposed by acid, the fatty acids were extracted with ether, the ether distilled off, and the oil (Substance *c*) distilled under diminished pressure. This distillation gave: *Fraction I* (0·2 gram), 212—215°/10 mm.; *Fraction II* (17·5 grams), 220—228°/10 mm.; *Fraction III* (9 grams), 250—258°/10 mm.; and *Fraction IV* (about 5 grams) remained behind as a tarry mass, which was not further examined.

Substance a.—The substance crystallised from 80 per cent. alcohol in small, glistening, white plates, which after two crystallisations melted sharply at 155°, and weighed 0·55 gram. The substance is insoluble in water, practically insoluble in cold alcohol, but soluble in the majority of the other organic solvents. It crystallises from chloroform in slender needles. When dissolved in chloroform, acetic anhydride and sulphuric acid give a greenish-blue colour, which afterwards changes to a deep rich green. In the same solvent sulphuric acid gives only a yellowish-orange colour, and the acid becomes fluorescent. On warming with concentrated nitric acid, a yellow product is obtained, which becomes brownish-red with ammonia. These reactions point to the substance being allied to, but not identical with, the phytosterols. For analysis the substance was dried at 100°:

0·1494 gave 0·4417 CO_2 and 0·1671 H_2O. $C=80·65$; $H=12·45$.

$C_{31}H_{58}O_2$ requires $C=80·52$; $H=12·55$ per cent.

In the polarimeter the substance is optically inactive. From either acetic acid or carbon disulphide solution it absorbs bromine rapidly.

Substance b.—After two crystallisations from dilute alcohol the substance melted at 120—122°. No special crystalline form was noticeable, the material merely separating as a white, flocculent mass from the solvent. As only 0·3 gram was obtained after crystallisation, attempts at further purification were impossible:

0·1168 gave 0·3501 CO_2 and 0·1121 H_2O. C=81·75; H=10·66.
$C_{29}H_{45}O_2$ requires C=81·88; H=10·58 per cent.

The substance absorbs bromine from carbon disulphide solution, gives no distinctive colour tests, such as Substance *a* gives, and generally speaking, is much less sharply defined than Substance *a*.

Substance c.—As described above, this material was distilled under 10 mm. pressure, and divided into four fractions:

Fraction (1).—When crystallised several times from alcohol, this melted at 61—62°. It showed no indication of unsaturation with the permanganate test. These facts, together with the boiling point, show the substance to consist of palmitic acid, occurring here owing to the sparing solubility of lead palmitate in ether.

Fraction (2).—A small quantity of palmitic acid occurring here as an impurity was separated by precipitation with magnesium acetate in alcoholic solution. The main bulk of the material recovered from solution gave an iodine value of 94, showed the elaidic acid reaction with nitrous acid, and had D^{14} 0·8975. Also 1 gram required 0·1961 gram of potassium hydroxide for neutralisation. The substance was therefore identified as oleic acid.

Fraction (3).—This distilled at 250—258°/10 mm., and solidified to a white, crystalline mass melting at 33—34°. It had an iodine value of 72·6, and 1 gram required 0·1499 gram of potassium hydroxide for neutralisation. It was thus identified as erucic acid.

Examination of Fraction B.

The fraction was distilled under 10 mm. pressure, and divided into three fractions, namely, (1) 4·5 grams boiling at 210—215° and solidifying to a white, crystalline mass, (2) about 0·25 gram boiling at 240—250°, and (3) tarry matter left behind.

The first fraction melted, after recrystallisation, at 62°, gave no iodine absorption, and 1 gram required 0·2180 gram of potassium hydroxide for neutralisation. The substance was therefore palmitic acid.

The second fraction was too small for thorough purification. It melted at 69—70° after recrystallisation, and the indications pointed to its being stearic acid.

The third fraction could not be purified, and was not worked up.

Summary.

There were thus separated from the crude fatty acids, palmitic acid (8·7 per cent.), oleic acid (36·1 per cent.), erucic acid (18·6 per cent.), together with small quantities of the neutral substances, $C_{31}H_{58}O_2$ and $C_{29}H_{45}O_2$, both probably of phytosterol nature. The alcoholic extract of dry mangel matter contained only a small quantity of oil and some protein matter.

The thanks of the author are due to Prof. T. B. Wood for the supply of the material and the interest he has taken in the work throughout.

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CXV.—*Latent Heats of Vaporisation of Mixed Liquids. Part III. Mixtures of Associated with Non-associated Liquids. New Criteria for the Detection of Solvates in Mixtures of Liquids.*

By DANIEL TYRER.

IN the previous papers (Trans., 1911, **99**, 1633; this vol., p. 81) the latent heats of binary mixtures were investigated for cases in which both constituents were normal, in the sense that they consisted of simple non-associated molecules. In the present paper cases are given in which one of the constituents of each mixture is a normal liquid and the other is an associated liquid. For such mixtures it is possible to determine from a study of their latent heats whether the associated constituent undergoes gradual dissociation as it is diluted with the other constituent, or whether a solvate is formed; but this will be explained in the later part of the paper.

For the methods of investigation, description of the apparatus, and explanations concerning the general terms employed, the previous papers must be consulted. The present paper will be confined to a general statement of the new results obtained and their discussion. The following four cases have been investigated: (1) benzene and ethyl alcohol; (2) chloroform and methyl alcohol;

(3) chloroform and acetone; (4) carbon tetrachloride and ethyl alcohol.

Benzene and Ethyl Alcohol.

The benzene used was prepared from Kahlbaum's purest material by refractionating over phosphoric oxide. A litre of it distilled without the boiling point varying by more than 0·02°. It boiled at 79·75°/750 mm., and had a specific volume of 1·13914 at 20·58°. The ethyl alcohol was prepared from "absolute" alcohol by distilling first over a little sodium, and then twice fractionating over metallic calcium. It boiled at 78·07°/747 mm., and had a specific volume of 1·26565 at 20·58°.

Latent Heat of Pure Ethyl Alcohol.

The following results have been obtained:

Temperature.	Pressure.	Latent heat.
78·07°	747 mm.	198·4
77·91	740 ,,	200·0
77·65	737 ,,	200·6
77·96	745 ,,	201·9
	Mean result at 78·12°/750 mm.	200·3

This result is somewhat lower than the numbers obtained by previous investigators, namely, Andrews, 202·4; Wirtz, 205·1; Brown, 216·4. It was noticed that if the alcohol were allowed to take up a little water from the air by exposure, its latent heat was considerably increased.

The results for the mixtures will be found in the tables given below:

Chloroform and Methyl Alcohol.

The pure chloroform was prepared in the same way as that used in a previous case (Trans., 1911, **99**, 1633).

The methyl alcohol was prepared in the same manner as the ethyl alcohol, from Kahlbaum's pure material. It boiled at 64·86°/757 mm., and had a specific volume of 1·26339 at 20·55°.

Latent Heat of Pure Methyl Alcohol.

The following results were obtained:

Temperature.	Pressure.	Latent heat.
64·45°	744 mm.	263·7
64·46	744 ,,	263·8
64·85	757 ,,	263·3
	Mean at 64·86°/757 mm.	263·4

Brown obtained the result 262·2; Andrews, 263·7, and Wirtz, 267·5.

Chloroform and Acetone.

The same specimen of chloroform was used as employed in the previous case. The pure acetone was obtained by refractionating the "pure" material from Kahlbaum. A litre distilled constantly to within 0·04°. It boiled at 55·97°/750 mm., and had a specific volume of 1·26260 at 20·52°.

Latent Heat of Pure Acetone.

The following results were obtained:

Temperature.	Pressure.	Latent heat.
55·53°	738 mm.	123·97
55·49	736 ,,	124·02
Mean at 55·97°/750 mm. ………		23·88

Carbon Tetrachloride and Ethyl Alcohol.

The samples of the substances used in this case had been used in previous cases, for which details have been given. The results for mixtures are given in the collected tables below.

Boiling Points of the Mixtures.

For each mixture investigated the boiling point was determined incidentally. These boiling points were all reduced to a standard pressure for each case by assuming that the effect of pressure on the boiling point of a mixture is approximately given by the additive law from the effects on the boiling points of the pure constituents. It was found that the case chloroform and acetone gave a maximum boiling point, whilst the other three cases gave minimum boiling points.

Latent Heats of Mixtures at Constant Pressure (L_p).

The results given in the following table have been read off from smoothed curves of experimental values for even compositions. The composition *C* is, in each case, the percentage of the constituent which has the greater specific gravity.

T is the boiling point of the mixture of composition *C*.

	Benzene and ethyl alcohol.		Chloroform and methyl alcohol.		Chloroform and acetone.		Carbon tetrachloride and ethyl alcohol.	
C.	*T* (750 mm.).	L_p.	*T* (757 mm.).	L_p.	*T* (750 mm.).	L_p.	*T* (745 mm.).	L_p.
0	78·12°	200·3	64·86°	263·4	55·97°	123·88	77·91°	200·3
10	74·40	175·3	64·05	209·5	57·00	121·2	74·82	141·8
20	71·86	156·9	62·38	177·5	57·79	117·8	72·44	120·3
30	70·26	144·3	60·68	154·7	58·83	114·0	70·25	106·0
40	69·00	139·1	59·07	137·8	59·91	109·1	68·35	95·5
50	68·41	134·3	57·52	122·8	61·03	103·2	66·64	88·1
60	67·97	130·2	55·94	110·2	62·19	95·3	65·32	83·2
70	67·76	126·1	54·52	99·5	63·41	86·4	64·42	80·9
80	68·20	122·6	53·66	91·4	63·84	79·0	63·88	77·5
90	69·54	116·0	53·65	84·2	62·02	73·1	64·30	[illegible]4·2
00	79·75	94·45	61·37	59·32	6[illegible]·25	59·34	75·92	[illegible]·85

In all cases the value of L_p shows a steady diminution with increase of the concentration.

The values for the constant boiling mixtures in the four cases are as follows:

	C.	T.	L_p.
(1) Benzene and ethyl alcohol	68·2	67·76°	126·8
(2) Chloroform and methyl alcohol	87·4	53·43	86·6
(3) Chloroform and acetone......................	78·0	63·93	80·1
(4) Carbon tetrachloride and ethyl alcohol..	84·2	63·86	76·1

Thayer (*J. Physical Chem.*, 1898, **2**, 382) found in case (1) C = 66·5, whilst Ryland (*Amer. Chem. J.*, 1899, **22**, 384) found C = 68, and Young and Fortey the value 67·6.

For case (2) Ryland found C = 88, and in case (3) he obtained the value C = 80, whilst Thayer (*J. Physical Chem.*, 1899, **3**, 36) found C = 81.

These values are rather considerably higher than those found by the author. It is, however, difficult to fix the point precisely from the boiling-point curve (as was done by Thayer), because a comparatively large change in the composition makes but a small change in the boiling point. This will be evident by reference to the boiling-point curve in Fig. 1.

Composition of the Vapour in Equilibrium with Liquid of known Composition.

In the following table are given the compositions of the vapours C_v in equilibrium with the liquids of composition C_L. The results given represent the "smoothed" values of the experimental figures:

C_L.	C_v. Benzene and ethyl alcohol.	C_v. Chloroform and methyl alcohol.	C_v. Chloroform and acetone.	C_v. Carbon tetrachloride and ethyl alcohol.
0	0	0	0	0
10	31·4	25·2	5·30	40·0
20	44·0	41·7	12·35	54·6
30	52·4	54·1	20·3	64·7
40	58·2	64·0	29·4	72·0
50	62·4	72·3	39·8	76·8
60	66·0	78·0	52·3	79·4
70	68·7	81·5	65·9	81·5
80	71·4	84·2	81·5	83·2
90	76·4	88·7	94·7	87·1
100	100·0	100·0	100·0	100·0

In the first, second, and fourth of the above cases it will be observed that at low compositions the vapour is richer in the heavier constituent than the liquid; but at the higher compositions the reverse is true. We find also a similar behaviour, although in the reverse order for the third case. It follows, therefore, that at some point the composition of liquid and vapour is the same. These points, which were read from the curve of vapour compositions, have already been given.

Latent Heats of Mixtures at Constant Composition (L_c).

The values of L_c can be calculated from the values for L_p in a manner previously described, provided we know the heat change which occurs when 1 gram of condensed vapour is added to a large amount of liquid with which the vapour was in equilibrium. As a rule these heat changes are very small. To determine whether they were negligibly small in the particular cases here investigated, some measurements were made for those mixtures with which the heat changes are greatest, and even with these they were found to be easily negligible. With acetone and chloroform it is true that a considerable amount of heat is evolved on mixing in the proportion roughly of 20 per cent. of the former, but it is just at this point that the composition of liquid and vapour are closest.

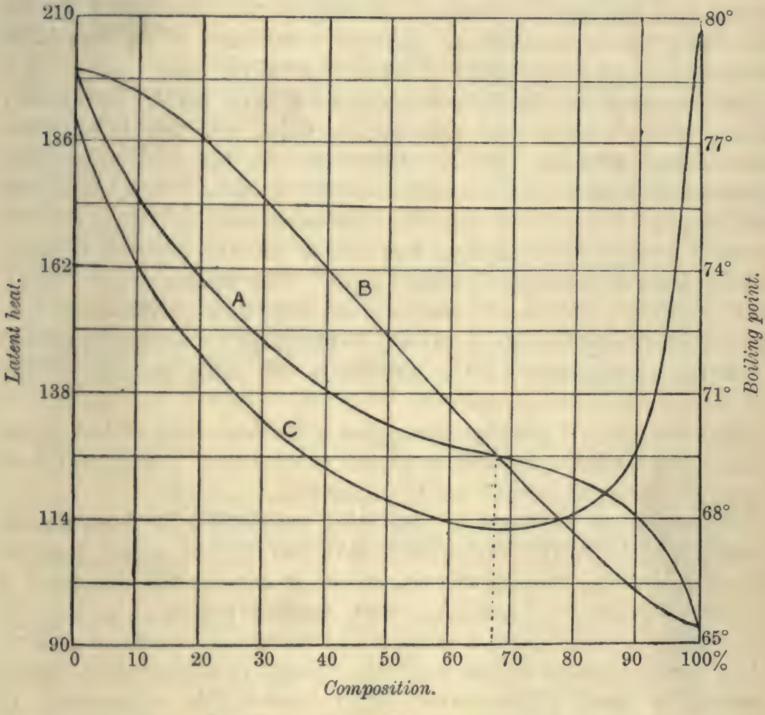
In the following table are given the latent heats at constant composition for the four cases investigated, together with the temperatures with which they correspond.

	Benzene and ethyl alcohol.		Chloroform and methyl alcohol.		Chloroform and acetone.		Carbon tetrachloride and ethyl alcohol.	
C.	*T.*	L_c.	*T.*	L_c.	*T.*	L_c.	*T.*	L_c.
0	78·12°	200·3	64·86°	263·4	55·97°	123·88	77·91°	200·3
10	77·36	195·8	65·21	242·3	57·48	119·1	77·58	186·0
20	76·20	188·3	64·48	221·0	58·78	114·1	77·08	171·5
30	74·68	176·7	63·60	200·6	59·97	108·9	76·23	157·0
40	72·66	163·9	62·56	180·2	61·05	103·1	75·02	141·7
50	70·67	150·6	61·28	161·6	61·99	96·8	73·36	127·2
60	68·84	137·4	59·76	143·4	62·88	90·2	71·32	112·5
70	67·92	124·5	57·96	125·2	63·66	83·7	68·92	97·7
80	70·29	111·6	55·13	104·0	63·92	78·1	65·13	82·5
90	73·10	101·0	53·72	80·0	53·50	72·3	64·80	67·1
100	79·75	94·45	61·37	59·32	61·25	59·34	75·92	46·85

Discussion of Results.

As already mentioned, three of the cases investigated exhibit minimum boiling points, and the other case gives a maximum boiling point. The existence of constant boiling mixtures causes an intersection of the two latent heat curves at the same composition as that of the constant boiling mixture. This is illustrated by the curves in Fig. 1, which represents as a typical case that of benzene and ethyl alcohol. It will be seen that the addition of a little benzene to pure ethyl alcohol causes a decrease in both latent heats, but the rate of diminution is the greater for the latent heat at constant pressure. On adding more benzene the curves begin to approach each other again until they intersect at the same composition as corresponds with the minimum boiling point. The intersection of the two curves means nothing more than that at this point liquid and saturated vapour have the same composition. The other three cases give quite similar sets of curves. It may be mentioned that in all four cases the graph of the latent heat at constant composition is very nearly a straight line.

FIG. 1.



A = *Composition*—L_p *curve.*
B = ,, —L_c ,,
C = ,, —*Boiling-point curve.*

Let us suppose that mixtures of benzene and alcohol consist simply of normal molecules of benzene and molecules of alcohol of various degrees of complexity. How then should the boiling point and latent heats vary with the composition? Now it follows from the fact that the vapour of boiling alcohol consists mostly of normal molecules, that dissociation of the associated molecules in the liquid would cause the boiling point to fall; that is, if by any means we could have a liquid consisting only of normal C_2H_6O

molecules, it would have a lower boiling point than ordinary alcohol. We may therefore regard a dilute solution of alcohol in benzene as a normal mixture of benzene and a liquid the boiling point of which is below 78°, and as the boiling point of a normal mixture is approximately a linear function of the composition, we should find that a dilute solution of alcohol in benzene has a boiling point much lower than that of either of the constituents; that is to say, the system will have a minimum boiling point. According to this reasoning, if no solvates are formed, a mixture of an associated with a non-associated liquid of which the boiling points are not too widely varying, should show a minimum boiling point. As already shown, if we have a minimum boiling point, the two latent heat curves must intersect. We see, therefore, that the supposition that no solvates exist in the mixture accounts, qualitatively at least, for the results obtained in the case discussed and similarly for the other two alcoholic mixtures, but not so for the acetone mixture which gives a maximum boiling point. The existence of a maximum boiling point in any mixture can only be regarded as indicative of the formation of a solvate, although it by no means follows that the composition of the solvate is the same as that of the maximum boiling mixture.

However, it will now be shown that a further study of the latent heats at constant composition proves conclusively that in all four cases solvates are formed in the mixtures.

The universal existence of molecular association in those liquids which contain a hydroxyl group have led to the belief that, in these cases, the process of association is due to the power of a hydroxyl group of combining with another hydroxyl group. If this idea is correct (and it seems to be widely accepted), it follows that the association of two hydroxyl groups is independent, qualitatively at least, of the nature of the rest of the molecules. In other words, when two hydroxyl substances are mixed or dissolved one in the other, solvates are always formed. This generalisation, although a simple consequence of the idea that molecular association in hydroxyl compounds is due to the combination of the hydroxyl groups, does not appear to have been fully recognised. It covers a wide region in aqueous solutions, for, with the exception of salts, the only large class of substances which are appreciably soluble in water contain hydroxyl groups.

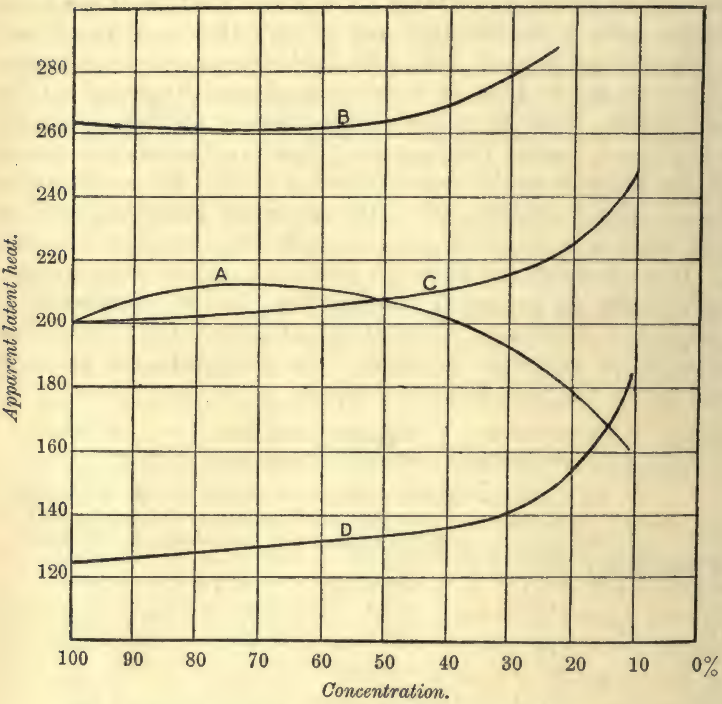
On the other hand, there is no theoretical reason for supposing that a hydroxyl group can attach itself to a molecule which contains no such group, and it therefore becomes of interest to test this point practically. The study of the latent heats of mixtures furnishes a trustworthy method of determining whether in such solutions or mixtures as are here dealt with, solvates are formed. It was pointed out in the previous paper (*loc. cit.*) that the latent heat at constant composition of a normal mixture is approximately a linear function of the composition. In other words, each constituent in the mixture apparently retains its own latent heat, unaffected by the presence of the other constituent. It will be clear, then, that by the aid of this rule, we can determine the latent heat of either constituent in a given mixture if we know the latent heat of the mixture and of the other constituent, and applying this to the cases dealt with in this paper, we can calculate the apparent latent heat of the associated constituent at various concentrations. Now if no solvates are formed in these mixtures, then the latent heat of the associated liquid in the mixture should gradually diminish as the concentration gradually diminishes owing to the progressive dissociation of the associated molecules, until at infinite dilution it becomes constant, indicating complete dissociation. If we find this not to be the case, then undoubtedly, to some extent, solvates are formed in the mixture. In the following table are given the calculated apparent latent heats of the associated constituents in the four mixtures. The composition is given in percentages of the pure associated liquid.

	Apparent latent heat.			
	Ethyl alcohol diluted with benzene.	Methyl alcohol diluted with chloroform.	Acetone diluted with chloroform.	Ethyl alcohol diluted with carbon tetrachloride.
100 (pure liquid)	200·3	263·4	123·88	200·3
90	207·1	262·6	125·7	201·4
80	211·8	261·4	127·8	202·7
70	212	261·1	130·1	204
60	210	261	132	205
50	207	264	134	208
40	201	269	136	211
30	195	279	141	216
20	180	283	153	225
10	160	266	189	249

The above values may only be regarded as approximate. Apart from deviations due to the approximate character of the method of calculation, the values are considerably affected, especially at the weaker concentrations by comparatively small errors in the latent heats of the mixtures. However, the general trend of the results is clear and well defined. This can best be seen by reference to Fig. 2, in which these results have been plotted against the concentrations. It will be seen that in no case is there a steady diminution of the apparent latent heat as would be expected from a gradual dissociation of the associated molecules, but, on the contrary, the latent heat in all cases, over a portion of the range at least, increases with increase of the dilution. This can have no other meaning but that solvates are formed in the mixtures.

It cannot be expected that the curves should show any similarity in form, for this depends, of course, on the relative amounts of the solvates formed and their heats of dissociation; and for this reason also, it is quite impossible to determine the composition of the solvates.

FIG. 2.



A = *Latent heat of ethyl alcohol diluted with benzene.*
B = ,, ,, *methyl* ,, ,, *chloroform.*
C = ,, ,, *ethyl* ,, ,, *carbon tetrachloride.*
D = ,, ,, *acetone diluted with chloroform.*

In the chloroform–acetone mixture evidence of the existence of a solvate has already been found by Dolezalek (*Zeitsch. physikal. Chem.*, 1908, **64**, 727) from a study of vapour pressures of the mixtures.

It is difficult to conceive the nature of the solvates formed in these cases. There can be no doubt that the strongly reactive character of the hydroxyl group is the determining factor. Although acetone does not contain a hydroxyl group, it behaves similarly to a hydroxyl substance, and the associative properties in both are due possibly to the tendency of the oxygen atom to become quadrivalent. The possibility of the combination of a hydroxyl substance with a non-associated substance is proved by the existence of such a compound as $CHCl_3,18H_2O$, which is formed by cooling to 0° a mixture of chloroform and water.

Summary.

Results are given for the boiling points, vapour compositions, latent heats at constant pressure, and latent heats at constant composition for the following mixtures:

(1) Benzene and ethyl alcohol; (2) chloroform and methyl alcohol; (3) chloroform and acetone; (4) carbon tetrachloride and ethyl alcohol.

It is found that case (3) gives a maximum boiling point, and the other three cases give minimum boiling points. At these points the latent heat at constant pressure is identical with the latent heat at constant composition.

From a study of the latent heats of such mixtures a trustworthy method is established, by which the existence of solvates in the mixtures can be detected. In all four cases investigated solvates are formed.

In conclusion, the author desires to state that much of the expense of this research has been defrayed by a Research Grant from the Chemical Society, for which the author expresses his thanks.

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CXVI.—*Azo-dyestuffs of the Triphenylmethane Group.*

By Arthur George Green and Rajendra Nath Sen.

Considerable interest attaches to dyestuffs containing two different chromophors in the molecule, as it has not yet been established whether the tinctorial properties of such compounds are dependent on an additive effect of the chromophors each acting separately, or whether one group may intensify the action of the other, or an entirely new effect be called forth by their combined action. It was thought that a particularly interesting example for the study of this point would be afforded by azo-derivatives of triphenylcarbinol containing the azo-group in the para-position with respect to the methane carbon atom.

A few azo-derivatives of the triphenylcarbinol group have long been known, but these, as, for instance, "azo-green," all belong to the meta-class, being obtained by combination of the diazo-compounds of *m*-aminoleucomalachite-green and its analogues with salicylic acid.*

As a convenient source of dyestuffs of the required type we have employed the easily obtainable phenetoleazobenzaldehydesulphonic acid, $OEt\cdot C_6H_4\cdot N_2\cdot C_6H_3(SO_3H)\cdot CHO$, the preparation of which we have described in a previous communication (Trans., 1910, **97**, 2243). This aldehyde condenses readily in cold concentrated sulphuric acid solution with salicyclic or 2-hydroxy-*m*-toluic acids. The triphenylmethane compounds (leuco) thus produced are, by reason of the presence of the azo-group, yellow dyestuffs. On oxidation with a sulphuric acid solution of nitrosyl sulphate they are converted into azotriphenylcarbinol compounds. The latter are well defined polygenetic dyestuffs, dyeing wool directly in red shades, and giving various colours with the different metallic mordants. The chromium lakes, which are black and possess a remarkable degree of fastness to fulling and light, can be produced directly on the woollen fibre by dyeing with the azotriphenylmethane dyestuff (leuco), and then boiling the wool with an acidified solution of dichromate. Both oxidation and combination with chromium then occur at once, the colour changing from yellow to maroon, and finally to black.

Dyestuffs of very similar tinctorial properties are obtained by employing in place of the above phenetoleazobenzaldehydesulphonic acid, the naphtholazobenzaldehydesulphonic acid,

$$OH\cdot C_{10}H_6\cdot N_2\cdot C_6H_3(SO_3H)\cdot CHO,$$

or the dihydroxynaphthaleneazobenzaldehydetrisulphonic acid,

$$C_{10}H_3(OH)_2(SO_3H)_2\cdot N_2\cdot C_6H_3(SO_3H)\cdot CHO,$$

which compounds are readily prepared by combining the diazo-compound of 4-aminobenzaldehyde-2-sulphonic acid with β-naphthol or dihydroxynaphthalene-3:6-disulphonic acid respectively. The leuco-dyestuffs (azotriphenylmethane compounds) obtained from the latter aldehydes dye wool in orange shades. The corresponding azotriphenylcarbinol compounds are bluish-red dyestuffs, giving violet-black chromium lakes; thus the substitution of a naphthalene nucleus for a benzene nucleus in the azo-portion of the molecule has had the usual effect of reddening (blueing) the shades obtained.

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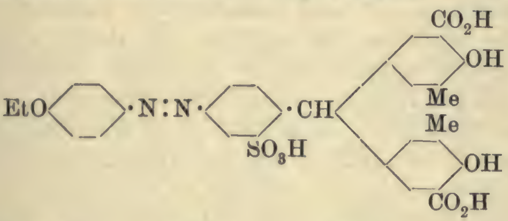
* Since the completion of this investigation in June, 1910, some para-azotriphenylmethane dyestuffs have been described by the Farbenfabriken vorm. Fr. Bayer & Co. in Eng. Pat. No. 2394 of 1910.

A comparison of the colour of the above dyestuffs and of their chromium lakes with that of analogous triphenylmethane compounds derived from salicylic and 2-hydroxy-*m*-toluic acids, but containing no azo-group, supports the conclusion that the tinctorial properties of these dyestuffs of mixed type is attributable to the additive effect produced by each chromophoric grouping acting independently. The above colouring matters appear to be the first members of the triphenylmethane group obtained which dye black shades.

*Condensation Product of Phenetoleazobenzaldehydesulphonic Acid with 2-Hydroxy-*m*-toluic Acid. Phenetoleazosulphophenyldihydroxyditolylmethanedicarboxylic Acid,*

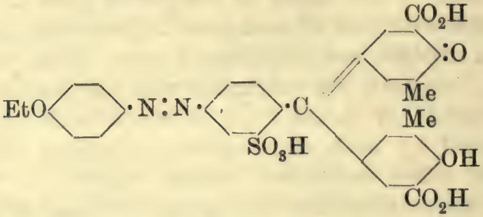


3·6 Grams of the azo-aldehyde were dissolved in 16 c.c. of cold concentrated sulphuric acid (free from nitric acid), to which were then added 3 grams of 2-hydroxy-*m*-toluic acid. The mixture was stirred until all was dissolved, and allowed to remain overnight at the ordinary temperature. It was then poured into about 300 c.c. of a mixture of ice and water, and the precipitate which separated was collected and washed. For purification it was dissolved in 500—600 c.c. of hot water, filtered from insoluble matter, and reprecipitated as an orange-red, crystalline powder by addition of concentrated hydrochloric acid. When redissolved in hot water with addition of some hydrochloric acid, it separated on cooling in fine, orange-red crystals. Yield, 4·6 grams:

0·188 gave 7·7 c.c. N_2 at 15° and 739 mm. N = 4·75.
0·410 ,, 0·166 $BaSO_4$. S = 5·55.
$C_{31}H_{28}O_{10}N_2S$ requires N = 4·52; S = 5·16 per cent.

The compound dyes wool from an acid bath in orange-yellow shades. On boiling the dyed wool in a solution containing potassium dichromate (3 or 4 per cent. on the weight of the wool) and sulphuric acid, the colour undergoes a striking series of changes passing from yellow through maroon to dark green and black.

Oxidation Product. Phenetoleazosulphophenyldihydroxyditolylcarbinoldicarboxylic Acid,

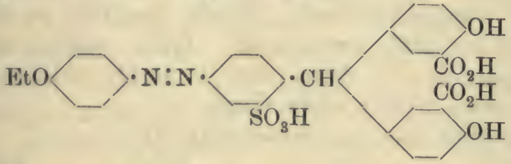


4·8 Grams of the azo-aldehyde dissolved in 20 c.c. of cold concentrated sulphuric acid were condensed with 4 grams of 2-hydroxy-*m*-toluic acid. The solution of the leuco-compound was then oxidised directly by addition of a solution of nitrosyl sulphate, prepared by slowly stirring 3 grams of finely powdered sodium nitrite into 25 c.c. of cold concentrated sulphuric acid. To complete the oxidation, the mixture was slowly warmed to 50° and kept at this temperature for an hour. After pouring into iced water the precipitated dyestuff was collected and washed. The product was dissolved in about 1200 c.c. of hot water, filtered from a small quantity of insoluble residue, and the clear filtrate, after cooling, precipitated by the addition of concentrated hydrochloric acid. It then separated in dark red, microscopic needles. Yield, 6·2 grams:

0·192 gave 7 c.c. N_2 at 16° and 745 mm. N = 4·30.
0·415 ,, 0·170 $BaSO_4$. S = 5·62.
$C_{31}H_{26}O_{10}N_2S$ requires N = 4·53; S = 5·18 per cent.

The compound dissolves in cold water, giving a red solution. In alkalis it dissolves with a bluish-red colour, and in concentrated sulphuric acid it also gives a red solution. It dyes wool from an acid bath in red shades, which on chroming become sage-green to black. With other mordants it produces the following shades: *Tin*, bright red; *copper*, bluish-maroon; *aluminium*, crimson to reddish-violet; *titanium*, brownish-red; *iron*, reddish-black. Wool dyed with the chromium lake exhibits an interesting series of colour changes when boiled with a solution of sodium hyposulphite. The greenish-black first becomes violet, presumably owing to the reduction of the azo-group and formation of the chromium lake of the *p*-aminotriphenylcarbinol dyestuff. On further reduction the violet is completely decolorised, and if the colourless wool retaining the leuco-compound is oxidised by boiling with a weak solution of potassium persulphate the violet colour is restored, but not the black. This formation of a violet colouring matter by partial reduction of a black would seem to be opposed to Scholl's rule (*Ber.*, 1903, **36**, 3410, 3426), according to which a deepening of the colour ("Vertiefung") is to be anticipated when in a compound containing two chromophors the reduction of one of them leads to the production of an auxochrome group. Probably the rule would have a wider validity if the words "shifting of the colour towards the violet" were substituted for "deepening of the colour."

Condensation Product of Phenetoleazobenzaldehydesulphonic Acid with Salicylic Acid. Phenetoleazosulphophenyldihydroxydiphenylmethanedicarboxylic Acid,



The condensation of the azoaldehyde with salicylic acid also occurs very readily. The product was a yellow dyestuff of similar appearance and properties to that from 2-hydroxy-*m*-toluic acid:

0·220 gave 9·3 c.c. N_2 at 18° and 758 mm. N=4·98.
0·477 „ 0·203 $BaSO_4$. S=5·84.
$C_{29}H_{24}O_{10}N_2S$ requires N=4·73; S=5·41 per cent.

It dyes wool yellow from an acid bath, and on treatment of the dyed wool with dichromate and sulphuric acid the shade is changed to black.

Oxidation to the azotriphenylcarbinol dyestuff is effected by means of nitrosyl sulphate in the manner described above, except that owing to the greater tendency for sulphonation to occur it is necessary to add about 10 per cent. of water to the sulphuric acid. The product is a red dyestuff similar to its higher homologue, and likewise possessing marked polygenetic properties.

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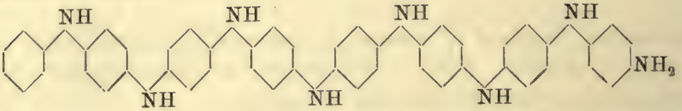
CXVII.—*Aniline-black and Allied Compounds. Part II.*

By Arthur George Green and Arthur Edmund Woodhead.

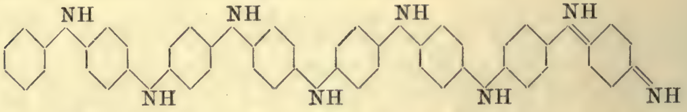
In a former communication (Trans., 1910, **97**, 2388) we have described and characterised a series of quinonoid derivatives of the colourless base leuco-emeraldine, which constitute the intermediate stages in the production of aniline-black. These primary products, two of which, namely, emeraldine and nigraniline, when formed on the fibre have long been known to technologists, are readily interconvertible by oxidation or reduction, and the results obtained by the quantitative determination of the oxygen or hydrogen consumed in passing from one stage to the other support the following constitutional formulæ for the respective compounds:

Leucoemeraldine:



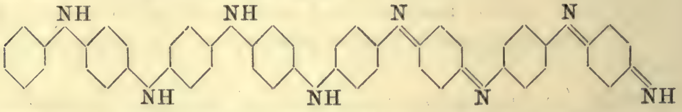
Colourless, amorphous base. Nearly insoluble in all solvents, including 80 per cent. acetic acid. High melting point. On exposure to air in the damp state is slowly oxidised to protoemeraldine, more rapidly when warm.

Protoemeraldine (monoquinonoid stage *):



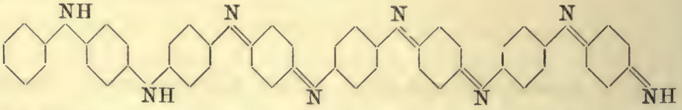
Violet base, forming yellowish-green salts. Soluble in 80 per cent. acetic acid with a grass-green colour.

Emeraldine (diquinonoid stage):



Violet-blue base, forming green salts. Soluble in 80 per cent. acetic acid and in 60 per cent. formic acid with a pure green colour. Dissolves in pyridine with a bright blue colour. Dissolves in pure concentrated sulphuric acid with a purplish-brown colour, and on dilution with water gives a bright green precipitate. The salts are stable, but the base is slowly oxidised by air to nigraniline base.

Nigraniline (triquinonoid stage):



Dark blue base, forming blue salts. Soluble in 80 per cent. acetic acid and in 60 per cent. formic acid with a pure blue colour, which on heating becomes green through reduction to emeraldine. Dissolves in pyridine with a bright blue colour. Dissolves in concentrated sulphuric acid with a violet colour, and on dilution with water gives a bright green precipitate of emeraldine sulphate The base is stable, but the salts are very unstable.

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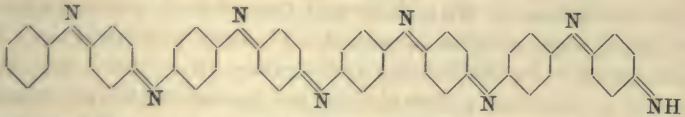
* In these formulæ, the position of the quinonoid groups is not yet established.

Pernigraniline (tetraquinonoid stage):



Purple base, forming purple salts. Soluble in 80 per cent. acetic acid with a violet colour. Both the base and its salts are very unstable, quickly undergoing degradation to the lower quinonoid stages with simultaneous production of decomposition products.

In our view, none of the above compounds can be regarded as "aniline-black," but they constitute, in fact, indamine-like intermediate stages in its formation. Apart from their colour, they differ from aniline-black in their greater instability, and give on reduction leuco-emeraldine, not easily oxidised by air, instead of a readily re-oxidisable leuco-black.

On the other hand, Willstätter and Dorogi (*Ber.*, 1909, **42**, 2147, 4118) have prepared a series of products which they term "aniline-blacks," by making use of methods not differing substantially from those employed by us to obtain emeraldine and nigraniline, except that the products formed were afterwards subjected to a prolonged treatment with dilute sulphuric acid with the object of removing mineral impurities. By extraction with 80 per cent. acetic acid we have been able to show that these "blacks" are, in fact, mixtures of emeraldine or nigraniline with polymerisation or decomposition products formed by the action of the acid used in the "purification" process. This conclusion was further confirmed by Green and Wolff (*Ber.*, 1911, **44**, 2570), who showed that by oxidising aniline with dichromate according to Willstätter and Dorogi's method, but without subjecting the product to subsequent "purification" with sulphuric acid, a compound was obtained entirely identical with our emeraldine, and completely soluble in 80 per cent. acetic acid, giving a bright green solution. After the acid treatment, however, the product (Willstätter and Dorogi's "bichromate-black") is only partly soluble in this solvent, and differs considerably from pure emeraldine.

To their so-called "aniline-blacks," Willstätter and Dorogi assign formulæ which are the same as those given by us to nigraniline and pernigraniline, although the main constituent of their products must be emeraldine or nigraniline respectively. The high state of oxidation assumed by these authors for their preparations is, moreover, opposed to the fact ascertained by us that under the influence of dilute acids the higher quinonoid stages readily become degraded to the lower stages, a fact which, although capable of ready demonstration, is also disputed by Willstätter.

The conclusions of Willstätter and Dorogi have received apparent verification from a series of analytical results published in a later communication by Willstätter and Cramer (*Ber.*, 1910, **43**, 2976), in which is described a new method for the estimation of quinonoid groups based on reduction with phenylhydrazine and the measurement of the nitrogen evolved. Green and Wolff (*loc. cit.*) have, however, shown that the results obtained by this method are only trustworthy provided the temperature required for reduction to the leuco-compound does not exceed 80—90°, for above this temperature auto-decomposition of the phenylhydrazine is liable to occur, and rapidly increases as the temperature is raised. Contrary to the statement of Willstätter and Cramer it was found that emeraldine and nigraniline are completely reduced to leucoemeraldine at temperatures considerably below 80° (even in the cold), and that the nitrogen evolved thereby corresponds with the formulæ previously assigned by us. At 150°, however, which is the final temperature employed by Willstätter and Cramer, the evolution of nitrogen becomes nearly continuous, and consequently the conclusions which these authors base on their results are invalidated.

In a subsequent communication (*Ber.*, 1911, **44**, 2162), Willstätter and Cramer have published the results of a repetition of our reduction experiments with titanium trichloride, obtaining figures which are in close accord with those previously obtained by us. As, however, these results do not agree with their own theoretical views or with their phenylhydrazine determinations, they fall back on the assumption that the end-product of the reduction with titanium trichloride in the cold or with phenylhydrazine below 150° is not the true leucoemeraldine, but the monoquinonoid stage, so that all the stages are thus raised by one. The extreme improbability of this assumption is apparent when it is considered that the reduction product is perfectly stable in presence of a large excess of the strong reducing agent, and further that the substance is almost colourless (brownish-white to greyish-white). The only experimental evidence advanced in its favour is the determination of the nitrogen evolved when the reduction product is heated with phenylhydrazine at 150°, which owing to the auto-decomposition of phenylhydrazine at this temperature must be considered invalid.

In order to place the matter beyond doubt, it seemed desirable to carry out quantitative reductions with *boiling* titanium trichloride on leucoemeraldine prepared from emeraldine by the action of phenylhydrazine at a low temperature. If this product is actually a monoquinonoid one, it would certainly undergo further reduction under these conditions, with a corresponding consumption of titanium trichloride. The results obtained justify the view that no reduction occurs, for the small consumption of hydrogen is not more than that accountable to aerial oxidation of the leuco-compound and to experimental error.

EXPERIMENTAL.

Emeraldine.

The preparation of the emeraldine employed was carried out substantially as previously described, but with some modifications in detail, which lead to a purer product. Aniline (144 gram) is suspended in water (3 litres), and carefully neutralised with hydrochloric acid (about 160 c.c. of 30 per cent. HCl). An excess of hydrochloric acid (93 c.c.) is further added, together with syrupy vanadium chloride (25 drops). When cold, the solution is mixed with a cold solution of sodium chlorate (84 grams) in water (600 c.c.), and the whole is kept in a refrigerator at a temperature of from 0° to 5° for about forty hours. The emeraldine hydrochloride formed is then collected, thoroughly washed with water, stirred with an excess of dilute ammonia in order to basify it, and again collected, and repeatedly washed with water. The emeraldine base thus obtained is free from nigraniline, and in the form of paste dissolves readily in 80 per cent. acetic acid, giving an almost clear, bright green solution. After drying at 100° it is less soluble, and becomes more insoluble at a higher temperature. If the base is exposed to air for a few days in the damp state, it becomes completely oxidised to nigraniline, and then gives a clear, blue solution in 80 per cent. acetic acid. The failure of Willstätter and Dorogi to obtain anything more than suspensions in this solvent is obviously due to the want of purity of their products, and this is further supported by their statement (*Ber.*, 1911, **44**, 2166) that the preparation obtained by them contained about 0·8 per cent. of ash before treatment with acid, whilst the ash in the emeraldine base prepared as above was less than 0·1 per cent. The presence of small quantities of acids or of salts prevents complete solubility, or causes the formation of a fine colloidal precipitate.

Leucoemeraldine.

The leucoemeraldine was prepared by the reduction of emeraldine in the undried condition at the ordinary temperature. The emeraldine paste obtained as above described was incorporated with an excess of phenylhydrazine in a mortar, the colour thereby changing from deep violet through slate-blue to a dirty white. For experiments with titanium trichloride the product was freed from excess of phenylhydrazine by washing with ether, and dried quickly on a porous plate. It still contained 49·42 per cent. of water. The percentage of chlorine in the dry product was found to be 0·73.

For ultimate analysis the base was completely freed from water by further washing with anhydrous ether, and then dried under diminished pressure at 50—70°. It formed a greyish-white powder, which became blue after a few hours' exposure to air, but could be kept unchanged in toluene containing a trace of phenylhydrazine. The following results were obtained on analysis *:

C(mean of three determinations) = 79·06; H(mean of three determinations) = 5·58; N(mean of two determinations) = 15·44.

$C_{48}H_{42}N_8$ requires C = 78·91; H = 5·75; N = 15·34 per cent.

Attempted Reduction with Titanium Trichloride.

A measured quantity of the standard titanium trichloride solution was run into a flask previously filled with carbon dioxide, and was heated to boiling. A weighed quantity of the moist leucoemeraldine (containing 50·58 per cent. of dry base) was then added, and the whole was boiled for five minutes. The contents of the flask were then rapidly cooled by immersion in iced water, and filtered when cold. All these operations were performed with a stream of carbon dioxide passing through the apparatus. An aliquot portion of the filtrate was then titrated with a *N*/10-solution of ferric ammonium sulphate. In two blank experiments made under these conditions 45 c.c. of the titanium trichloride solution required 24·12 c.c. of the *N*/10-ferric solution.

I. 1·0222 Grams of moist leucoemeraldine (containing 50·58 per cent. of dry base) and 45 c.c. of titanium trichloride required 20·5 c.c. *N*/10-ferric solution. The difference between this figure and the blank experiment is 3·5 c.c., which represents a consumption of hydrogen of 0·00035 gram for the amount of leucoemeraldine taken, or of 0·00059 gram for 1 gram of dry leucoemeraldine.

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* The numbers are corrected for chlorine (0·73 per cent.).

II. 1·0795 Grams of moist leucoemeraldine (50·58 per cent.) and 45 c.c. of titanium trichloride required 19·8 c.c. of the *N*/10-ferric solution. The difference between this figure and the blank experiment is 4·32 c.c., which represents a consumption of hydrogen of 0·00043 gram for the amount of leucoemeraldine taken, or of 0·00077 gram for 1 gram of dry leucoemeraldine.

III. 1·7270 Grams of moist leucoemeraldine (50·58 per cent.) and 45 c.c. of titanium trichloride required 16·92 c.c. of *N*/10-ferric solution. The difference between this figure and the blank experiment is 7·2 c.c., which represents a consumption of hydrogen of 0·00072 gram for the amount of leucoemeraldine taken, or of 0·00083 gram for 1 gram of dry leucoemeraldine.

The increasing value of the hydrogen consumption for each successive experiment is due to the progressive oxidation of the leucoemeraldine by exposure to air between the experiments.

The hydrogen consumption required by theory for a monoquinonoid compound is 0·00275 gram for 1 gram of substance, that is, more than three times the highest figure obtained.

Taken in conjunction with our previous results, the following conclusions are arrived at:

(1) The product formed by reduction of emeraldine or nigraniline with titanium trichloride or phenylhydrazine in the cold is leucoemeraldine, $C_{48}H_{42}N_8$, a colourless base devoid of quinonoid groups.

(2) Protoemeraldine is the monoquinonoid stage.

(3) Emeraldine is the diquinonoid stage.

(4) Nigraniline is the triquinonoid stage.

(5) Pernigraniline is the tetraquinonoid stage.

(6) The "blacks" of Willstätter and his pupils are not true "aniline-blacks," but are mixtures of emeraldine or nigraniline with products of their decomposition or polymerisation. They should therefore be removed from the literature as chemical individuals.

Our thanks are due to Mr. S. Wolff for the preparation of the emeraldine employed in these experiments.

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CXVIII.—*The Rotatory Powers of the* d- *and* l-*Methylethylphenacylthetine Salts.*

By Clara Millicent Taylor.

Although substances of which the optical activity can be associated with the presence of an asymmetric quadrivalent sulphur atom have been known for some twelve years, the literature concerning them is sparse, and the quantitative data concerning their rotation constants is slight in amount (Pope and Peachey, Trans., 1900, **77**, 1072; Smiles, *ibid.*, 1900, **77**, 1174; Pope and Neville, *ibid.*, 1902, **81**, 1552). At the suggestion of Professor Pope I have therefore prepared the methylethylphenacylthetine bromide of Smiles in quantity, and, after resolving it into its optically active components with the aid of *d*-α-bromocamphor-π-sulphonic acid, determined the rotation constants of several of the carefully purified salts of the optically active bases with more accuracy than has been hitherto found possible. The values of the constants now given may thus be regarded as replacing those previously recorded.

The *d*- and *l*-methylethylphenacylthetine *d*-α-bromocamphor-π-sulphonates were prepared as described by Smiles and by Pope and Peachey, with the exception that both salts were recrystallised from alcohol until no further change in their rotatory power was observed.

d-*Methylethylphenacylthetine* d-α-*Bromocamphor*-π-*sulphonate.*

This salt crystallises in long, colourless needles melting at 180—181°. The following determinations of rotatory power were made in 4-dcm. tubes at 20°, the weight of salt stated being made up to 30 c.c. with the solvent:

0·1809 gram in water.

	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.
α......	+ 1·75°	+ 1·48°	+ 1·44°
$[\alpha]$ ...	72·5	61·3	59·7

0·1830 gram in water.

	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.
α......	+ 1·73°	+ 1·49°	+ 1·44°
$[\alpha]$ ...	70·9	61·1	59·0

0·2835 gram in water.

α......	+ 2·70°	+ 2·30°	+ 2·24°
$[\alpha]$ ...	71·4	60·8	59·2

0·2421 gram in alcohol.

α......	+ 2·71°	+ 2·28°	+ 2·17°
$[\alpha]$ ...	83·9	70·6	67·2

0·3102 gram in alcohol.

α......	+ 3·46°	+ 2·93°	+ 2·74°
$[\alpha]$ ...	83·6	70·8	66·2

Mean values in aqueous solution.

$[\alpha]$...	+71·6°	+61·1°	+59·3°
[M]..	362	308	300

Rotatory dispersions: In water, $\text{Hg}_{\text{green}}/\text{Na}_{\text{yellow}} = 1{\cdot}207$; $\text{Hg}_{\text{yellow}}/\text{Na}_{\text{yellow}} = 1{\cdot}030$. In alcohol, $\text{Hg}_{\text{green}}/\text{Na}_{\text{yellow}} = 1{\cdot}255$; $\text{Hg}_{\text{yellow}}/\text{Na}_{\text{yellow}} = 1{\cdot}059$.

It is noteworthy that the rotatory dispersions in aqueous solutions are appreciably smaller in magnitude than those observed in alcohol.

l-*Methylethylphenacylthetine* d-*α-Bromocamphor-π-sulphonate.*

This salt forms colourless needles melting at 196°, and gave the following results on determination of the rotation constants:

	0·0777 gram in water.				0·1454 gram in water.		
	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.		Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.
α ……	+ 0·59°	+ 0·50°	+ 0·48°		+ 1·09°	+ 0·92°	+ 0·90°
[α] …	56·9	48·3	46·3		56·2	47·4	46·4
	0·2282 gram in water.				0·3569 gram in water.		
α ……	+ 1·74°	+ 1·46°	+ 1·40°		+ 2·74°	+ 2·26°	+ 2·23°
[α] …	57·2	48·0	46·0		57·6	47·5	46·9
	0·0576 gram in alcohol.				0·0960 gram in alcohol.		
α ……	+ 0·56°	+ 0·47°	+ 0·44°		+ 0·91°	+ 0·78°	+ 0·72°
[α] …	72·9	61·2	57·3		71·1	60·9	56·2
	0·1160 gram in alcohol.				Mean values in aqueous solution.		
α ……	+ 1·11°	+ 0·94°	+ 0·88°	[α] …	+ 57·0°	+ 47·8°	+ 46·4°
[α] …	71·8	60·8	56·9	[M]..	287·7	241·3	234·3

Rotatory dispersions: In water, $\text{Hg}_{\text{green}}/\text{Na}_{\text{yellow}} = 1{\cdot}228$; $\text{Hg}_{\text{yellow}}/\text{Na}_{\text{yellow}} = 1{\cdot}029$. In alcohol, $\text{Hg}_{\text{green}}/\text{Na}_{\text{yellow}} = 1{\cdot}265$; $\text{Hg}_{\text{yellow}}/\text{Na}_{\text{yellow}} = 1{\cdot}073$.

The arithmetic sums of the corresponding molecular rotatory powers for the *d*-α-bromocamphor-π-sulphonates of *d*- and *l*-methylethylphenacylthetine in the dilute aqueous solutions dealt with should be twice the molecular rotatory powers of the acidic ion; the arithmetic differences should be twice the molecular rotatory powers of the basic ion. A comparison can thus be instituted between the values for the acidic ion obtained by Pope and Read (Trans., 1910, **97**, 2201) from the examination of the ammonium salt and those deducible from the values now given; the numbers are given below:

		Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.
Acidic ion	Pope and Read ……	346·5°	295·2°	278·7°
	From the thetine …	324·6	274·8	266·9
Basic ion	From the thetine …	36·9	33·5	32·6

		$\text{Hg}_{\text{green}}/\text{Na}_{\text{yellow}}$.	$\text{Hg}_{\text{yellow}}/\text{Na}_{\text{yellow}}$.
Acidic ion	Pope and Read………	1·243°	1·059°
	From the thetine……	1·216	1·029
Basic ion.	From the thetine……	1·133	1·027

The considerable discrepancies between the molecular rotatory powers and rotatory dispersions as deduced from the ammonium salt and the thetine salts of the optically active acid is noteworthy; in connexion therewith attention may be called to the observation made by Pope and Read (this vol., p. 760) that the molecular rotatory powers of salts of the type *dAlB* are frequently normal, whilst those of the salt *dAdB* are abnormal. The numbers given above also show that the rotatory dispersions of the optically active thetine ion exhibit low values.

d- *and* l-*Methylethylphenacylthetine Picrates.*

These salts, obtained as before described, crystallise from acetone in straw-yellow coloured prisms melting at 128—129°; the following determinations of rotatory power were made in acetone solutions at 20°:

	d-*Methylethylphenacylthetine Picrate.*			l-*Methylethylphenacylthetine Picrate.*		
	0·1724 gram in 30 c.c. in 4-dcm. tube.			0·1438 gram in 30 c.c. in 4-dcm. tube.		
	$\mathrm{Hg_{green}}$.	$\mathrm{Hg_{yellow}}$.	$\mathrm{Na_{yellow}}$.	$\mathrm{Hg_{green}}$.	$\mathrm{Hg_{yellow}}$.	$\mathrm{Na_{yellow}}$.
α......	+ 0·36°	+ 0·31°	+ 0·28°	− 0·32°	− 0·27°	− 0·25°
$[\alpha]$ ...	15·7	13·5	12·2	16·7	14·1	13·0
	0·2138 gram in 30 c.c. in 4-dcm. tube.			0·2846 gram in 30 c.c. in 4-dcm tube.		
α......	+ 0·45°	+ 0·39°	+ 0·34°	− 0·60°	− 0·53°	− 0·47°
$[\alpha]$ ...	15·8	13·7	11·9	15·8	14·0	12·4
	0·4393 gram in 25 c.c. in 2-dcm. tube.			0·6868 gram in 25 c.c. in 2-dcm. tube.		
α......	+ 0·56°	+ 0·48°	+0·43°	− 0·89°	− 0·76°	− 0·69°
$[\alpha]$ ...	15·9	13·6	12·2	16·2	13·8	12·6

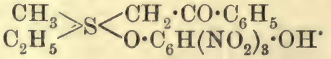
The mean values for the rotation constants are as follows:

		$\mathrm{Hg_{green}}$.	$\mathrm{Hg_{yellow}}$.	$\mathrm{Na_{yellow}}$.
$[\alpha]$......	+ or −	16·0°	13·8°	12·4°
[M] ...	+ or −	67·7	58·3	52·4

Rotatory dispersions: $\mathrm{Hg_{green}}/\mathrm{Na_{yellow}} = 1·290$; $\mathrm{Hg_{yellow}}/\mathrm{Na_{yellow}} = 1·113$.

It is to be observed that the rotatory dispersions for the picrate are larger than those for the basic ion in aqueous solution stated above.

d- *and* l-*Methylethylphenacylthetine Styphnates,*



$$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>\!S\!<\!\begin{matrix}CH_2{\cdot}CO{\cdot}C_6H_5\\O{\cdot}C_6H(NO_2)_3{\cdot}OH\end{matrix}$$

On addition of a concentrated aqueous solution of sodium styphnate to one of the *d*-*α*-bromocamphor-*π*-sulphonate of either *d*- or *l*-methylethylphenacylthetine, the styphnate of the organic base is deposited as a yellow, crystalline precipitate; the salts are purified by recrystallisation from moist acetone, and form straw-coloured, transparent prisms melting at 119—120°:

0·1845 *d*-thetine salt gave 14·5 c.c. N_2 at N.T.P. N = 9·90.
0·1452 *l*-thetine salt „ 11·6 c.c. N_2 at N.T.P. N = 10·06.
$C_{17}H_{17}O_9N_3S$ requires N = 9·56 per cent.

The following determinations of rotatory power were made, the weights stated being made up to 30 c.c. with acetone, and examined at 20° in 4-dcm. tubes:

d-*Methylethylphenacylthetine Styphnate.*

	Hg$_{green}$.	Hg$_{yellow}$.	Na$_{yellow}$.
	0·1875 gram.		
α	+ 0·29°	+ 0·25°	+ 0·23°
[α]......	11·6	10·0	9·2
	0·2726 gram.		
α	+ 0·42°	+ 0·37°	+ 0·33°
[α]......	11·6	10·2	9·1

l-*Methylethylphenacylthetine Styphnate.*

	Hg$_{green}$.	Hg$_{yellow}$.	Na$_{yellow}$.
	0·2050 gram.		
α	− 0·33°	− 0·29°	− 0·27°
[α]......	12·1	10·6	9·9
	0·3296 gram.		
α	− 0·54°	− 0·47°	− 0·44°
[α]......	12·3	10·7	10·0

The mean values for the rotation constants are as follows:

		Hg$_{green}$.	Hg$_{yellow}$.	Na$_{yellow}$.
[α]	+ or −	11·9	10·4	9·5
[M] ...	+ or −	52·1	45·5	41·8

Rotatory dispersions: Hg$_{green}$/Na$_{yellow}$ = 1·246; Hg$_{yellow}$/Na$_{yellow}$ = 1·086.

Optical Inversion of d- *and* l-*Thetine Salts.*

On allowing the colourless solutions of the *d*-α-bromocamphor-π-sulphonates of *d*- and *l*-methylethylphenacylthetine to remain at the ordinary temperature, they become slightly yellow, but no change in rotatory power is to be observed. On heating the two salts in aqueous solution on the water-bath for an hour the solutions acquire the molecular rotatory powers of the acidic ion, and on subsequently treating the solutions with picric acid the externally compensated picrate melting at 123° is obtained; it is to be concluded that the optical inversion is due, not to decomposition of the quadrivalent sulphur compound, but to its dissociation. Similarly, on decomposing the optically active platinichlorides, suspended in water, by a current of hydrogen sulphide in the cold, an optically active solution results, which becomes optically inactive when heated on the water-bath. If the solution of the thetine hydrochloride thus obtained is evaporated on the water-bath, an oily residue remains, which yields the externally compensated picrate on treatment with sodium picrate.

It is therefore concluded that although the quadrivalent sulphur compound is a comparatively stable base, it readily undergoes dissociation, and that the dissociation, just as in the case of the asymmetric optically active quaternary ammonium compounds (Trans., 1901, **79**, 828), leads to the disappearance of the optical activity due to the basic ion.

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CXIX.—*The Conversion of* d-*Glucosamine into* d-*Glucose.*

By James Colquhoun Irvine and Alexander Hynd, M.A., B.Sc. (Carnegie Fellow).

All attempts to effect the apparently simple change of converting glucosamine into the corresponding hexose have hitherto proved unsuccessful, although the problem has been vigorously attacked by many workers during the thirty-four years which have elapsed since the discovery of the amino-sugar by Ledderhose.

It is now well known that although the theoretical amount of nitrogen is evolved when glucosamine is decomposed by nitrous acid, the product of the change is not a simple hexose, but the hydrated furan derivative known as chitose. Chitose is, in fact, formed under all conditions when nitrous acid acts on glucosamine, and this accounts for the alternative name "chitosamine," which was for some time applied to the amino-compound. Even the modification of the nitrous acid reaction adopted by Fischer, in which glucosamine hydrochloride is shaken with the equivalent amount of silver nitrite, leads to no different result, and the literature on the chemistry of glucosamine contains numerous references to other attempts to eliminate the amino-group without inducing internal dehydration in the sugar molecule.

Apparently the only example of the conversion of glucosamine into a definite derivative of glucose is the experiment quoted by Tiemann (*Ber.*, 1886, **19**, 50), in which he isolated phenylglucosazone from the amino-sugar. The yield obtained is, however, not stated, and was apparently small; the melting point observed was inconclusive, and, in addition, the formation of the osazone still leaves open the possibility that glucosamine may be derived from mannose, and not from glucose; in fact, the constitution at present assigned to glucosamine, which represents it as an α-amino-derivative of *d*-glucose, depends almost entirely on the synthesis of the compound from *d*-arabinose (Fischer and Leuchs, *Ber.*, 1903, **36**, 24), and the stereochemical arrangement of the amino-group is thus uncertain.

As chitose results from the dehydration of a hexose, it seemed possible that its formation could be avoided by the substitution of the hydroxyl groups in glucosamine, while leaving the amino-group unaltered. A substituted glucosamine of this nature should react normally with nitrous acid, and be converted into a derivative of the parent hexose, provided the reaction proceeded without a change of the nature of the Walden inversion taking place.

The results of an investigation based on the above considerations have already been published by us in a paper (Trans., 1911, **99**, 250), in which we gave an account of the preparation of triacetylmethylglucosamine and methylglucosamine from bromotriacetylglucosamine. By a coincidence, some of the results then described were duplicated in a paper by M. L. Hamlin, which appeared a few weeks later (*J. Amer. Chem. Soc.*, 1911, **33**, 766). We communicated with Mr. Hamlin, who has since abandoned his work on these derivatives of glucosamine, and left us to complete the research outlined in our original paper.

One of the important questions then left unsettled was the possible identity of the methylglucosamine, prepared from bromotriacetyl glucosamine, with the aminomethylglucoside obtained by Fischer and Zach from dibromotriacetylglucose (*Ber.*, 1911, **44**, 132). As then pointed out, the identity of the two compounds would mean the completion of a series of reactions resulting in the direct synthesis of glucosamine from glucose. We have accordingly repeated the preparation of methylglucosamine, modifying the process as explained in the experimental part, so as to obtain only one stereochemical form, and have prepared pure specimens of the hydrochloride and hydrobromide. These salts display the most striking similarity to Fischer's compounds in crystalline form, solubility, and rotatory power.

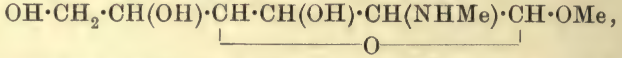
	Methylglucosamine hydrochloride.	Aminomethylglucoside hydrochloride.	Methylglucosamine hydrobromide.	Aminomethylglucoside hydrobromide.
Decomposition temperature ...	190°	215°	181°	205°
$[\alpha]_D^{20°}$ in water	−24·2	−25·1	−20·2	−21·2
$[\alpha]_D^{20°}$ in methyl alcohol	−16·6	—	−14·8	—

The decomposition points now recorded for our hydrochloride and hydrobromide are 25° lower than those quoted by Fischer, although the rotatory powers are now shown to be practically identical. The two aminoglucosides are, however, definitely isomeric, and we are indebted to Professor Emil Fischer, to whom we sent a specimen of our hydrochloride, for a critical comparison of the compound with the similar salt of his aminoglucoside. He reports that the decomposition point of methylglucosamine hydrochloride is depressed from 190° to 172° by mixing with an equal amount of the hydrochloride of aminomethylglucoside, and emphasises the different behaviour of the two salts when heated with acids. In parallel experiments the hydrochlorides were heated to 100° with 25 per cent. hydrochloric acid. In six minutes the solution of the aminomethylglucoside salt was yellow, and in ten minutes became distinctly brown. The corresponding solution containing methylglucosamine hydrochloride remained meanwhile quite colourless, and this difference in stability became more emphatic on heating for forty-five minutes.

The isomerism thus established is consistent with the formation from bromotriacetylmethylglucoside of the interesting series of anhydro-sugar derivatives recently described by Fischer and Zach (*Ber.*, 1912, **45**, 456). Methylglucosamine is thus an α-aminomethylhexoside, and, as the compound is here shown to be a derivative of glucose, it may now be termed *α-aminomethylglucoside.* In Fischer's aminomethylglucoside, on the other hand, the amino-group may occupy the β-, δ-, or ε-position.

The conversion of α-aminomethylglucoside (methylglucosamine) into methylglucoside cannot be carried out directly, as the action of nitrous acid gives uncrystallisable syrups which reduce Fehling's solution and resemble chitose. The decomposition of triacetylmethylglucosamine by nitrous acid is equally unsatisfactory, owing to the removal of the acetyl groups by hydrolysis. Internal dehydration of the sugar molecule can thus only be prevented by the introduction of stable residues into all the hydroxy-positions before any attempt is made to remove the amino-group by means of nitrous acid.

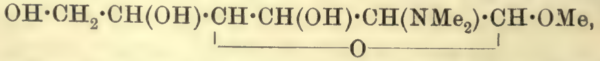
With this end in view, we subjected α-aminomethylglucoside to methylation by the silver oxide reaction. The alkylation presented unusual difficulties, and two distinct reactions occurred simultaneously. Part of the glucoside underwent normal methylation, only the hydroxyl groups being substituted; but the bulk of the material was converted into α-monomethylaminomethylglucoside,



$$OH\cdot CH_2\cdot CH(OH)\cdot \underbrace{CH\cdot CH(OH)\cdot CH(NHMe)\cdot CH}_{O}\cdot OMe,$$

which combined with the silver iodide formed to produce an additive compound, $C_8H_{17}O_5N,AgI$. This product was insoluble in alcoholic methyl iodide, and thus separated in the course of the methylation. It proved to be exceedingly stable, and was only decomposed into its constituent molecules by boiling with water.

The methylation effected in each treatment with the alkylating mixture was thus very slight, owing to the separation of material from solution as soon as the equivalent amount of silver iodide had been formed, and no fewer than nine successive alkylations were required to produce α-dimethylaminomethylglucoside,



$$OH\cdot CH_2\cdot CH(OH)\cdot \underbrace{CH\cdot CH(OH)\cdot CH(NMe_2)\cdot CH}_{O}\cdot OMe,$$

It was thus obviously impracticable to extend the methylation to the hydroxyl groups, and, of course, the use of nitrous acid was also precluded. Fortunately, it was possible to expel the alkylamino-group from the dimethylaminomethylglucoside by heating with barium hydroxide, the compound differing in this respect from the unsubstituted aminoglucoside, which is remarkably stable to alkalis. This reaction gave methylglucoside as the essential product, but as the compound could not be made to crystallise, it was completely methylated, and tetramethyl methylglucoside was finally obtained pure by fractional distillation.

The removal of the methyl groups was effected in two stages. On hydrolysis with dilute acid, tetramethyl glucose was obtained, and its identity confirmed by analysis, melting point (85—86°), and by the specific rotation in water ($[\alpha]_D + 82{\cdot}1°$). To complete the series of reactions, the alkylated sugar was converted into the parent hexose by heating with a 45 per cent. solution of hydrogen iodide at 94°. *d*-Glucose, showing the permanent specific rotation $+52{\cdot}4°$, was thus obtained in good yield, and its identity confirmed by conversion into the phenylosazone, which possessed the correct melting point (208°) and specific rotation ($-49{\cdot}2°$ in alcohol).

The conversion of glucosamine into glucose is thus possible through the following reactions:

d-Glucosamine hydrochloride ⟶ bromotriacetylglucosamine hydrobromide ⟶ triacetylaminomethylglucoside hydrobromide ⟶ aminomethylglucoside hydrochloride ⟶ methylaminomethylglucoside ⟶ dimethylaminomethylglucoside ⟶ [methylglucoside] ⟶ tetramethyl methylglucoside ⟶ tetramethyl glucose ⟶ *d*-glucose.

The constitution of some of the intermediate compounds in the above scheme shows certain unexpected irregularities, and the main result of the research can only be accepted as a proof that glucosamine is a derivative of glucose after consideration of each of the reactions involved. This is detailed in the discussion which follows.

Discussion of Results. Constitution of Glucosamine.

Relationship of Glucosamine to Glucose.—The critical reaction in the conversion of glucosamine into glucose is the decomposition of dimethylaminomethylglucoside by treatment with barium hydroxide, as all the other reactions employed appear to proceed without disturbing the stereochemical relationships of the groups involved; thus, as already shown (*loc. cit.*), bromotriacetylglucosamine, triacetylaminomethylglucoside, and α-aminomethylglucoside are all to be regarded as true derivatives of glucosamine, and the silver oxide method of methylation does not appear to have any effect on configuration, save when applied to reducing sugars. In such cases β-glucosides are produced in greater proportion than is represented by the equilibrium mixture of the sugar originally present, but this factor may be disregarded in the reactions now under review, as the methylations were conducted on stable glucosides. Moreover, we find that alkali hydroxides are incapable of effecting the change $\alpha \rightleftarrows \beta$ in the methylglucosides, as 1 per cent. solutions of α- and β-methylglucoside in 3*N*-sodium hydroxide underwent no appreciable alteration in rotatory power when heated to 100° for five hours.

The inquiry is thus limited to the question of whether, in displacing the substituted amino-group from dimethylaminomethylglucoside, a Walden inversion occurs in the α-asymmetric system. We are of the opinion that this change does not take place, but no rigid proof can be offered, as it may be admitted that the displacement of any group by any other group may be accompanied by inversion. Indirect evidence has, however, been obtained that the change in question proceeds without alteration of configuration. The asymmetric system involved is comparable with that which is affected in the conversion of gluconic acid into mannonic acid by heating with pyridine bases. This reaction is, of course, reversible, and an equilibrium mixture results. No case is, in fact, known where the inversion of the α-asymmetric system in a sugar is complete, and no recorded case can be found of the conversion of a glucoside of one sugar directly into a glucoside of another sugar without preliminary removal of the glucosidic group.* In other words, it is possible to pass from methylglucoside to a mixture of methylmannoside and methylglucoside, but only after hydrolysis, subsequent action of alkali on the sugar formed, and condensation with methyl alcohol.

Presumably, then, even if it were possible for inversion to take place in the reaction now under discussion, a mixture of methylglucoside and methylmannoside would be formed. We have, however, clear proof that such is not the case. Methylmannoside, if present, would participate equally with methylglucoside in all the subsequent reactions; but the fully methylated hexoside finally obtained showed the same optical activity in aqueous as in alcoholic solution. Tetramethyl methylglucoside is the only known hexoside which displays this property, the rotation of the mannosides being notably increased in the dextro-sense by solution in alcohol (Trans., 1905, **87**, 1462). Further, the hydrolysis of the alkylated hexoside was carried out under the same conditions as those previously adopted for tetramethyl methylglucoside (Trans., 1904, **85**, 1049), and the rotation changes were observed at the same time intervals. On plotting the results thus obtained, the curve coincided with that previously determined, the end-points were identical, and agreed with the calculated values. Tetramethyl glucose is thus the sole active product of the change, and no alkylated mannose was present.

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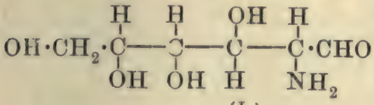
* The observation quoted by Fischer (*Ber.*, 1895, **28**, 1154), that α-methylgalactoside is converted into an amorphous isomeride by concentration of a methyl-alcoholic solution in presence of dilute acid, may constitute an exception to the above statement. The compound thus formed seems to be the glucoside of a feebly dextrorotatory aldose (Irvine and Cameron, Trans., 1905, **87**, 907), but no analogous change has been observed by us in the methylglucosides or methylmannoside.

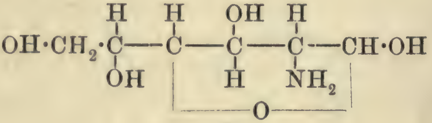
We therefore conclude that our results establish the relationship between glucosamine and glucose, and that the former is to be regarded as *a*-amino-*d*-glucose. Two alternative formulæ may thus be adopted for the compound:



$$\mathrm{OH\cdot CH_2\cdot}\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}\text{—}\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}\text{—}\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}\text{—}\overset{\mathrm{H}}{\underset{\mathrm{NH_2}}{\mathrm{C}}}\mathrm{\cdot CHO}$$

or

(I.)



(*a* and *β*).

(II.)

Hitherto the aldehydic formula has received support, as glucosamine displays doubtful mutarotation, and does not form glucosides by the usual methods. The absence of mutarotation, however, constitutes no objection to formula II, considering that glucosamine is strongly basic, and liberates ammonia in aqueous solution. The equilibrium between two γ-oxidic forms might thus be instantaneously established. On the other hand, the additive salts of glucosamine show well-marked mutarotation, and previous failure to prepare glucosides from glucosamine is due entirely to the sparing solubility of the hydrochloride in alcohols. The existence of *a*-aminomethylglucoside and of other aminoglucosides prepared from glucosamine * disposes of the second objection to formula II, which is therefore suggested, subject to the modification afterwards developed.

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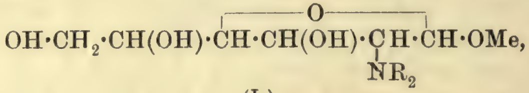
* Several glucosides derived from glucosamine have now been prepared and will be described in a forthcoming paper. The list includes the ethyl-, amyl-, benzyl-, and menthyl-aminoglucosides, aminohelicin, aminosalicin, and morphine *a*-aminoglucoside.

Constitution of α-Aminomethylglucoside and its Homologues.

Generally speaking, the properties of α-aminomethylglucoside and its *N*-alkyl homologues justify the adoption of the simple formula



$$OH\cdot CH_2\cdot CH(OH)\cdot \overbrace{CH\cdot CH(OH)\cdot \underset{NR_2}{CH}\cdot CH}^{O}\cdot OMe,$$

(I.)

where R = the methyl group or hydrogen. In many respects, however, the properties of the compounds show such remarkable divergencies from those to be expected from the above structure that modification of the formula seems necessary. As such modification affects the question of the constitution of glucosamine, the argument is here given in detail.

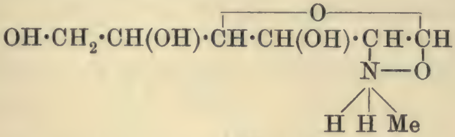
In the first place, the hydrolysis of α-aminomethylglucoside by means of hydrogen chloride proceeds with unusual difficulty. The compound is practically unaffected by heating with 5 per cent. hydrochloric acid at 100°, and requires an acid concentration of 40 per cent. for complete hydrolysis. Determinations of the rates of hydrolysis of glucosides carried out by E. F. Armstrong (*Proc. Roy. Soc.*, 1904, **74**, 188) show that the α- and β-methylglucosides are more stable than any of the other compounds examined by him. As shown below, the rate of hydrolysis of α-aminomethylglucoside, if compared according to Armstrong's numerical method with that of other simple glucosides, indicates that the compound is quite unique.

Glucoside.	Comparative rate of hydrolysis.	
α-Aminomethylglucoside	1 (approx.)	
α-Methylglucoside	100	E. F. A. (*loc. cit.*)
β-Methylglucoside	180	
Salicin	600	
Maltose	740	

On the other hand, Fischer's isomeric aminomethylglucoside is very easily hydrolysed by acids, although quantitative data are lacking.

The stability of α-aminomethylglucoside thus resembles that shown by the chloraloses, and suggests the presence of a double ring in the sugar molecule. The stability is also intimately connected with both the presence and position of the nitrogen atom, as shown by the remarkable fact that dilute nitrous acid, even in the cold, gives a product which has a vigorous action on Fehling's solution. The glucosidic part of the molecule thus seems to be affected whenever the amino-group is attacked.

These considerations point to the existence of a structure resembling the betaine ring, in which the glucosidic methoxyl group is attached through the nitrogen atom in the manner shown below:

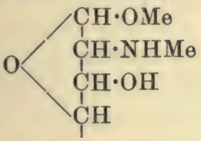


(II.)

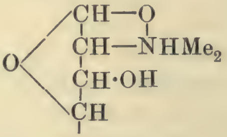
This constitution is supported by the behaviour of the compound towards alkalis. When heated to 160° with concentrated sodium hydroxide, both ammonia and methylamine were produced, thus indicating the connexion between nitrogen and the methyl group. α-Aminomethylglucoside, in the form of the free base at least, seems, in fact, to react according to both formulæ I and II, and this would also account for the two simultaneous types of methylation undergone by the compound. Further evidence, pointing to the same conclusion, is afforded by the study of the mono- and dimethyl-aminomethylglucosides. Both compounds are difficult to hydrolyse, and react as very feeble bases. When decomposed with alkalis they appear to give mixtures of amines. Again, the tendency of these compounds to form molecular complexes with silver iodide is another feature bringing them into line with betaine, which gives a series of similar additive compounds with metallic halides, and with the alkylated *iso*-oximes described by Dunstan and Goulding (Trans., 1901, **79**, 631).

The two alkylaminomethylglucosides thus appear to react both as normal glucosides and as *N*-cyclic compounds, the essential part of the structures being:

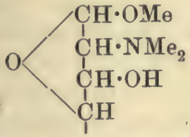
Monomethylaminomethylglucoside,



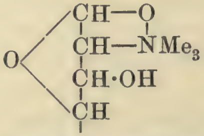
and



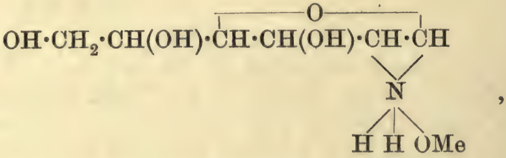
Dimethylaminomethylglucoside,



and



One discordant reaction, however, has to be recorded. When decomposed by hydrogen iodide, monomethylaminomethylglucoside gives two molecular proportions of methyl iodide, and dimethylaminomethylglucoside similarly gives three molecules of methyl iodide. These results, which were obtained in the course of Zeisel estimations, suggest the presence of two and three methoxyl groups respectively. Such, however, is not the case, as there can, at the most, be only one methoxyl group united to carbon, and the possible number of N·OMe groups is also limited to one; thus, *a*-aminomethylglucoside might conceivably be capable of reacting in the form

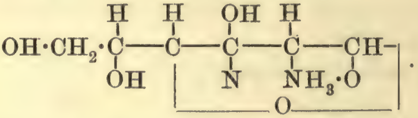


$$OH\cdot CH_2\cdot CH(OH)\cdot \overset{|}{C}H\cdot CH(OH)\cdot CH\cdot \overset{|}{C}H \quad (\text{—O—}) \qquad \underset{H\ H\ OMe}{N},$$

but it is difficult to see, in view of the combustion results obtained, how its mono- and di-methyl homologues could contain more than one methoxyl group linked to nitrogen.

At the same time we find that the group NMe is not reduced by hydrogen iodide under the conditions of the Zeisel process, as we obtained negative results on applying the analytical method to mono- and di-methylaniline, salts of dimethylamine, trimethylamine, and betaine, and also to ethyliminoglucose.* In the meantime this behaviour must be left unexplained, but we have commenced a research on the synthesis of compounds containing the grouping $NMe_2\cdot\dot{C}H\cdot\dot{C}H\cdot OMe$, in order to study their behaviour towards hydrogen iodide.

Extending these considerations to the structure of free glucosamine, a new formula for the base is indicated:



$$OH\cdot CH_2\cdot\underset{OH}{\overset{H}{C}}—\overset{H}{C}—\underset{N}{\overset{OH}{C}}—\underset{NH_3\cdot O}{\overset{H}{C}}—CH— \quad (\text{—O—}).$$

This constitution is suggested merely tentatively, and is, of course, confined to reactions of the free base only. We are now undertaking experiments to test its application. It appears to explain in a satisfactory manner most of the reactions of glucosamine, including the absence of mutarotation, the formation of the phenylcarbimide derivative, and the molecular dehydration of the latter. The production of *d*-glucosone from glucosamine hydrochloride is also explicable in terms of the formula, and, above all, the fact that glucosamine tetrabenzoate has no reducing action, and, nevertheless, is unacted on by nitrous acid, affords considerable support to the view. At all events, the methyl homologues of glucosamine are capable of reacting according to the above general structure, which may reasonably be extended to the parent base in view of the acidic nature of the terminal ·CH·OH group in reducing sugars. A betaine-like structure for glucosamine derivatives may also help to explain the natural formation of betaine, particularly as chitin, from which glucosamine is derived, has recently been detected by E. O. von Lippmann as a constituent of beet juice (*Ber.*, 1911, **44**, 3716).

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* The description of this compound has not yet been published.

EXPERIMENTAL.

To facilitate description, it should be stated that throughout the work all evaporations and concentrations were conducted under diminished pressure. All solvents and reagents were pure and dry.

α-Aminomethylglucoside.

The preparation of this compound under the name methylglucosamine has already been described (*loc. cit.*). The process has now been considerably modified and improved. There is no necessity to use pure bromotriacetylglucosamine hydrobromide, as the crude compound, when freed from hydrogen bromide, answers sufficiently well. The condensation to a glucoside must, however, be carried out without delay as the unpurified bromo-compound is highly unstable. The reaction should also be carried out with small quantities of material as described below:

15·5 Grams of bromotriacetylglucosamine hydrobromide (dried under diminished pressure) are extracted with 100 c.c. of anhydrous methyl alcohol, and filtered from glucosamine hydrobromide. If the directions originally given for preparing the bromo-compound are strictly adhered to, the filtrate contains a constant amount (12 grams) of the acetylated derivative. A solution of 7·5 grams of dry morphine dissolved in 200 c.c. of methyl alcohol is then quickly added and the liquid cooled. In a few minutes the separation of morphine hydrobromide begins, and may be promoted by stirring. After an hour the solution is filtered, and, on evaporation to half its bulk at 30°, a small second crop of the morphine salt crystallises out. This is removed, and the further treatment of the filtrate is as described in our previous paper. The yield is 10 grams. The use of morphine possesses obvious advantages over the pyridine method formerly employed.

It is, moreover, unnecessary to isolate the acetylated aminoglucoside before removing the acetyl groups. The concentrated alcoholic solution of the compound, referred to above, is mixed with a methyl-alcoholic solution of hydrogen chloride so as to give a 2 per cent. solution of acid on diluting with the alcohol to

250 c.c. The liquid is then boiled under a condenser for three hours, neutralised by shaking successively with lead carbonate and silver carbonate, filtered, decolorised by shaking with charcoal, and evaporated to a syrup. On extraction with methyl alcohol and evaporation, a small quantity of morphine aminoglucoside * separates, which is removed by filtration. The filtrate contains α-aminomethylglucoside, which may be converted into either the hydrochloride or the hydrobromide by the addition of the requisite amount of the halogen acid dissolved in dry alcohol, and subsequent precipitation with ether. The yield of free base is 4·5 grams. In all, 20 grams of the aminoglucoside were prepared by this method.

Aminomethylglucoside Hydrochloride.—The constants of the compound were redetermined for reasons given in the introduction. When systematically recrystallised as described, the purest crop decomposed sharply at 190·5° (corr.), and this value remained constant after three subsequent purifications. As the same result was obtained with the product of a second preparation, and also with that from the pyridine method previously described, this value represents the correct decomposition point. The temperature of decomposition was not affected by heating for two hours at 80°/15 mm. over phosphoric oxide.

The specific rotation in water was determined for a concentration approximating to that employed by Fischer and Zach (*loc. cit.*):

Solvent.	c.	l.	α_{20°.	$[\alpha]_D^{20^\circ}$.
Water	8·9580	1	−2·17°	−24·22°
Methyl alcohol	2·7030	1	0·45	16·65

Aminomethylglucoside Hydrobromide.—Difficulty was experienced in obtaining this salt quite white, and, even after repeated precipitation from ethyl-alcoholic solution by the addition of ether, the compound softened indefinitely between 80° and 100°. After drying at 60°/15 mm. over phosphoric oxide, the purest crops were dissolved in methyl alcohol, ether was cautiously added, and the liquid decanted from the oily precipitate thus formed. The hydrobromide subsequently separated from the solution in well-formed needles. The process was repeated until the decomposition point was quite sharp. The value found, after drying as described at 60°, was 181° (corr.):

Solvent.	c.	l.	α_{20°.	$[\alpha]_D^{20^\circ}$.
Water	2·423	1	−0·49°	−20·23°
Methyl alcohol	2·572	1	0·38	14·78

Found: Br = 29·13; OMe = 12·68.

$C_6H_{12}O_4N(OMe),HBr$ requires Br = 29·16; OMe = 11·31 per cent.

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* See footnote to p. 1133.

Action of Nitrous Acid on α-Aminomethylglucoside.

A 5 per cent. aqueous solution of the free base (1 mol.) was mixed with a similar solution of nitrous acid (1½ mols.), prepared from silver nitrite by exact decomposition with hydrogen chloride. After the evolution of nitrogen ceased, the solution was evaporated to dryness at 40°/15 mm. The syrupy residue was free from nitrogen, but reduced Fehling's solution vigorously. The reducing action was only eliminated by heating with excess of methyl alcohol containing 0·25 per cent. of hydrogen chloride for thirteen hours at 100°, and was thus due to hydrolysis of the glucosidic group. On working up the solution in the usual way, a neutral glucosidic syrup remained. This product, which failed to crystallise, could not be identified, and, judging from its behaviour on acetylation, did not contain any methylglucoside.

Action of Alkali Hydroxides on α-Aminomethylglucoside.

No alkaline vapours were evolved when a solution of the aminoglucoside in saturated aqueous barium hydroxide was kept at the boiling point. The use of 2*N*-sodium hydroxide in a similar experiment disengaged only small quantities of ammonia, and the bulk of the glucoside was recovered unaltered. A 6 per cent. solution of the glucoside in 7*N*-sodium hydroxide was then distilled, the volume being kept constant, until the evolution of alkaline vapours ceased. The odour of methylamine was then distinctly recognisable, and the hydrochlorides obtained on absorbing the evolved gases in acid contained, judging from the solubilities, methylamine hydrochloride. The decomposition of the aminoglucoside was, however, incomplete.

Finally, the compound was decomposed by heating to 160° for four hours with solid sodium hydroxide and a small quantity of water. The gas evolved again contained methylamine, but, contrary to expectation, the decomposition of the glucoside was imperfect, and no methylglucoside could be detected on working up the product.

This remarkable stability towards alkalis is considerably reduced by methylation of the amino-group.

Methylation of α-Aminomethylglucoside.

The alkylation was, in the first instance, carried out exactly as in the case of methylglucoside, the proportions being: aminomethylglucoside (1 mol.), methyl iodide (6 mols.), and silver oxide (3 mols.). The reaction at first proceeded normally, but, in a short time, the silver oxide adhered to the bottom of the flask as a plastic layer. The solution was accordingly diluted with excess of methyl alcohol until the oxide was loosened, and the mixture then boiled for six hours. Very little alcohol was required in the second methylation to effect complete solution in the methyl iodide. In the third and final alkylations no extraneous solvent was necessary, and the product was accordingly extracted with ether. The extract contained only a small quantity of a colourless syrup, which distilled under diminished pressure with a considerable amount of decomposition. The distilled liquid reacted strongly alkaline, behaved as a glucoside towards Fehling's solution, and evolved nitrogen when treated with nitrous acid. These properties show that normal methylation had taken place, but the small yield obtained made it impracticable to prepare the substance in quantity.

Methylation of the Amino-group.—The additive compound of aminomethylglucoside with silver iodide is formed in the course of the methylation just described, and this accounts for the poor yield and also for the cementing of the silver residues. A better method of preparing the alkylaminomethylglucoside is to methylate aminomethylglucoside by the modified process described for glucoseanilide (Trans., 1908, **93**, 1429).

Eight grams of the free base, dissolved in methyl alcohol, were mixed with methyl iodide (6 mols.), and silver oxide (3 mols.) gradually added. The flask was cooled externally, and fitted to an upright condenser whilst the mixture was stirred mechanically for six hours. Thereafter the temperature was raised to 30° for ten hours, and the mixture allowed to remain for three days. This treatment prevents cakeing of the silver oxide. The extracting agent was methyl alcohol, and, in the subsequent operations, the temperature was never allowed to exceed 30°.

The process was repeated, exactly as described, during a second alkylation. The syrup thus obtained was very soluble in methyl alcohol, only 6 c.c. being required to effect solution in the 37 grams of methyl iodide necessary for the third alkylation. In this reaction the silver oxide was converted into hard lumps, and the same result was more pronounced during the fourth, fifth, and sixth alkylations, which were conducted in methyl iodide solution. The essential products of the methylation at this stage are: (1) the additive compound, $C_8H_{17}O_5N,AgI$, which remains behind in the silver residues, and (2) a soluble syrup which consists of a mixture of mono- and di-methylaminomethylglucosides, the former being in excess.

α-Monomethylaminomethylglucoside.

The silver residues from the first six alkylations were united. Although mainly composed of granular silver iodide, a quantity of hard, cement-like material was present. The mass was finely powdered in an agate mortar, and boiled with water until the extracts were no longer alkaline. The bulky aqueous filtrate was evaporated to dryness at 50°/15 mm., the residue extracted with cold acetone, the solution filtered and evaporated to dryness. A clear yellow syrup (5 grams) remained, which crystallised readily. After spreading on a tile to remove the dimethylaminoglucoside, the compound was purified by solution in alcohol and precipitation with dry ether. After two such treatments the substance was obtained pure in the form of small, waxy leaflets. A specimen dried at 70°/15 mm. over phosphoric oxide was analysed.

Found: C=46·40; H=8·35.

$C_8H_{17}O_5N$ requires C=46·33; H=8·27 per cent.

As at least one of the two methyl groups present is attached to nitrogen, it is necessary to report the results of the Zeisel estimations in terms of methyl, and not as methoxyl:

0·1726 gave 0·3756 AgI. Me=13·92.

$C_6H_{11}O_5NMe_2$ requires Me=14·50 per cent.

The molecular weight, determined by the ebullioscopic method in alcoholic solution, was 218. (Calc., 207.)

The constitution of the compound was shown by the fact that one of the methyl groups was removed on hydrolysis, and is thus attached in the glucosidic position. The remaining methyl group must be attached to nitrogen, as the latter was not eliminated on treatment with nitrous acid, an oily nitrosoamine being then precipitated.

α-Methylaminomethylglucoside is readily soluble in water, acetone, or alcohol, sparingly so in benzene or ethyl acetate, and insoluble in pure ether. The crystals melt sharply at 89—90° to a colourless liquid, which decomposes at 215°. The compound behaves as a glucoside towards Fehling's solution, is practically neutral to litmus, and does not form definite salts with acids. The following observations on the rotatory power were made:

Solvent.	*c.*	*l.*	α_{20°.	$[\alpha]_D^{20^\circ}$.
Methyl alcohol	2·0005	2	−0·60°	−14·95°
Water	2·0002	2	0·52	12·99

Hydrolysis of α-Methylaminomethylglucoside.—The compound is practically unaffected by boiling with dilute aqueous hydrogen chloride. After three hours' heating in boiling water with a large excess of the concentrated acid, the solution was evaporated to dryness and kept for some time at 100° under diminished pressure. The residue was extracted with methyl alcohol, decolorised with charcoal, and again evaporated. The product was a colourless, uncrystallisable syrup showing all the properties of a reducing sugar. A Zeisel estimation on a specimen dried at 60°/15 mm. over phosphoric oxide showed that although the removal of the glucosidic group was not quite complete, the product of the hydrolysis is essentially methylaminoglucose.

Found: Me = 8·9.

$C_6H_{12}O_5NMe$ requires Me = 7·8 per cent.

Formation of the Additive Compound, $C_8H_{17}O_5N,AgI$.—With the object of definitely tracing the source of methylaminomethylglucoside and of ascertaining why methylation is almost entirely confined to one position in the molecule, 2 grams of the methylaminomethylglucoside were dissolved in 9 grams of methyl iodide (6 mols.), and treated with 7 grams of silver oxide (3 mols.). The silver oxide gradually caked together, and the mixture was kept gently boiling for six hours. The product was extracted with acetone, and on removal of the solvent, a brown syrup remained. This, on the addition of methyl alcohol, was converted into a pale yellow solid, which softened when heated under the alcohol, but became hard and compact when cold. After powdering and washing with alcohol it was obtained quite white. The compound decomposed, after preliminary softening, at 74°, was insoluble in the ordinary organic solvents, and when boiled with water was completely decomposed, yellow silver iodide* being left undissolved and methylaminomethylglucoside passing into solution. A small quantity of the dimethylaminoglucoside was also detected in the aqueous solution:

4·40 gave 2·35 AgI. AgI = 53·41.

$C_8H_{17}O_5N,AgI$ requires AgI = 53·13 per cent.

a-Dimethylaminomethylglucoside.

The soluble syrup obtained as already described after six alkylations of aminomethylglucoside consists of a mixture of mono- and di-methylaminomethylglucosides. The alkylations were therefore continued in methyl iodide solution. In each case a large proportion of the material escaped alkylation, owing to the formation of silver iodide compounds. After the ninth methylation, the total product was extracted with acetone, the solvent removed, and the residual syrup washed with ether to remove higher methylated products. The undissolved residue when shaken with alcohol gave the double compound of dimethylaminomethylglucoside and silver iodide as a pale yellow, microcrystalline powder. (Yield, 4·5 grams.) An additional yield of 4·2 grams was obtained by methylating pure methylaminomethylglucoside. The total product was decomposed by extraction with boiling water, the weight of silver iodide thus formed corresponding with molecular proportions of iodide and glucoside:

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* The silver iodide obtained in methylations is nearly black, even when the conversion of oxide into iodide is complete.

4·12 gave 2·20 AgI. AgI = 53·4.

$C_9H_{19}O_5N,AgI$ requires AgI = 51·47 per cent.

The aqueous extract of the glucoside was evaporated at 50°/15 mm., and gave *a*-dimethylaminomethylglucoside as a colourless syrup.

Found: C = 48·61; H = 8·53; Me = 19·52.

$C_6H_{10}O_5NMe_3$ requires C = 48·82; H = 8·66; Me = 20·37 per cent.

The compound, which is readily soluble in organic solvents, showed all the characteristics of a glucoside, but was only hydrolysed with difficulty. It is practically neutral in reaction, does not form definite salts, and is decomposed by heating with alkalis. Nitrous acid is without action on the compound.

Decomposition of a-Dimethylaminomethylglucoside by Barium Hydroxide.

Four grams of the glucoside were dissolved in 20 c.c. of a saturated aqueous solution of barium hydroxide, and heated for several hours at 100°. The alkylamines thus formed were removed by concentration of the liquid at 40°/15 mm. The evaporation was repeated until the distillates were no longer alkaline. The barium hydroxide was removed by carbon dioxide, the filtrate evaporated to dryness, extracted with methyl alcohol, and the solution again evaporated. The clear brown syrup thus obtained was essentially *a*-methylglucoside, but contained some undecomposed dimethylaminoglucoside, which could not be removed, owing to the failure of the material to crystallise. The mixture was accordingly re-methylated as afterwards described.

Decomposition by Sodium Hydroxide.—In an experiment duplicate with the above, 3*N*-sodium hydroxide was substituted for barium hydroxide. The amines liberated were converted into hydrochlorides, and, from their solubilities and behaviour towards nitrous acid, trimethylamine was present in addition to dimethylamine. The alkaline liquor was exactly neutralised with hydrochloric acid, decolorised with charcoal, and evaporated to dryness. The organic product was isolated by extraction with ethyl alcohol, evaporation to dryness, and re-extraction with the same solvent. A syrup was thus obtained which, on the addition of acetone, deposited a small, crystalline crop, which proved to be dimethylamine hydrochloride. The acetone filtrate on evaporation gave a small quantity of a clear syrup, resembling methylglucoside in solubilities and in its ready hydrolysis with hydrochloric acid. The specific rotation (+63°), methoxyl content (OMe=22 per cent.), and the behaviour towards concentrated alkali showed that some unaltered dimethylaminomethylglucoside was still present. The material was used, along with that described above, in the following methylation.

Methylation of the Syrup containing Methylglucoside.

The total weight of syrupy impure methylglucoside at this stage was 4·35 grams. The methylation was carried out exactly as previously described in the preparation of tetramethyl methylglucoside (*loc. cit.*), and thus the dimethylaminomethylglucoside present was left behind in the silver residues. After the customary three methylations the product was isolated and distilled in a vacuum, the whole of the volatile material being collected in one fraction so as to obtain any alkylated mannoside which may have been present. (Yield, 1·65 grams.)

As the distillate was coloured, it was hydrolysed by means of hydrochloric acid, the methylated sugar isolated as usual, and again re-alkylated. This procedure has frequently been found serviceable in the preparation of pure methylated sugars, and applies equally well to mannosides as to glucosides. The product, which consisted of a mixture of α- and β-tetramethyl methylglucosides, boiled at 128—130°/10 mm.

Found: C=52·66; H=8·84.

$C_{11}H_{22}O_6$ requires C=52·77; H=8·86 per cent.

The specific rotation in water and in alcohol were practically identical ($[\alpha]_D$ 84·2°).

Removal of the Methyl Groups from Tetramethyl Methylglucoside.

The glucosidic methyl group was eliminated by hydrolysis as previously described (Trans., 1904, **85**, 1065; 1905, **87**, 906). The usual rise and fall in rotatory power was observed. The curve representing the optical changes showed that the reaction proceeded quantitatively, and agreed well with that formerly established for this hydrolysis, but only the significant figures need be quoted:

$$\underbrace{\overset{\text{Initial }[\alpha]_{D}.}{+92^\circ}\qquad\qquad\overset{\text{Maximum }[\alpha]_{D}.}{+113^\circ}}_{\text{Rise}=21^\circ}\;\underbrace{\qquad\qquad\overset{\text{Final }[\alpha]_{D}.}{+77\cdot5^\circ}}_{\text{Fall}=35\cdot5^\circ}$$

The value found for the final specific rotation is identical with that found on hydrolysing pure tetramethyl methylglucoside. As the final value obtained on hydrolysing the corresponding mannoside is $+2\cdot5^\circ$, it follows that the latter was entirely absent, as less than 0·5 per cent. could be detected by the polarimetric method.

The hydrolysis product, isolated in the usual way, crystallised completely without vacuum distillation. After recrystallisation from petroleum of low boiling point, the following observations were made on the tetramethylglucose obtained.

Found: $OMe = 52\cdot1$; m. p. 85—86°; $[\alpha]_D$ in water $+82\cdot1^\circ$.

Tetramethylglucose requires $OMe = 52\cdot5$ per cent.; m. p. varies from 83° to 88°; $[\alpha]_D$ in water $+83\cdot3^\circ$.

Conversion of Tetramethyl Glucose into d-*Glucose.*

In this reaction it is desirable to remove the methyl groups under conditions which diminish the risk of racemisation or the conversion of the sugar formed into humic acid or the accompanying by-products.

A series of experiments, carried out in the Zeisel apparatus, showed that the removal of the methyl groups from tetramethyl glucose takes place quantitatively with all concentrations of hydriodic acid varying from 59 to 29 per cent., the temperature of decomposition meanwhile ranging from 80° to 114°. The conditions finally adopted were the following: Two grams of the methylated sugar were introduced into the decomposition flask of a Zeisel apparatus, and mixed with 22·5 c.c. of hydriodic acid (D 1·70) and 7·5 c.c. of water. The initial concentration of acid was thus 45 per cent. Reaction proceeded steadily at 95°, and the methyl iodide was continuously removed by a current of carbon dioxide. After heating for ten hours the evolution of the iodide ceased. The contents of the flask were diluted with water, filtered through asbestos, and shaken with lead carbonate. After filtration, the neutralisation was completed with silver carbonate, the liquid again filtered, and saturated with hydrogen sulphide. The small precipitate of silver sulphide was removed, the filtrate concentrated at 50°, decolorised with animal charcoal, and evaporated to a syrup at 30°/15 mm.

The residue was then extracted with boiling ether to remove a trace of undecomposed methylated sugar, dissolved in alcohol, filtered from traces of sulphur, and finally evaporated to a syrup. The product was dried at 60°/15 mm. until constant, and analysed. (Found, $C=39\cdot93$; $H=6\cdot68$. $C_6H_{12}O_6$ requires $C=40\cdot00$; $H=6\cdot66$ per cent.)

The permanent specific rotation in aqueous solution was for $c=1\cdot65$; $[\alpha]_D^{20}+52\cdot47°$.

The identity of the sugar with *d*-glucose was further confirmed by conversion into the phenylosazone, which, after crystallisation from aqueous pyridine, melted at 208° (corr.), and showed $[\alpha]_D^{20}-49\cdot2°$ in absolute alcohol. All the constants determined are thus in exact agreement with the standard values for *d*-glucose and glucosephenylosazone respectively.

The authors desire to express their indebtedness to Professor Emil Fischer for comparing the salts of the isomeric aminomethylglucosides; to the Carnegie Trust for a grant in aid of the investigation, and to Mr. Alexander W. Fyfe, M.A., for zealous assistance given in the course of the work.

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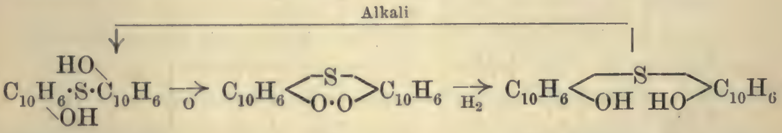
CXX.—*The Two Sulphides of β-Naphthol.*

By Cecil Reginald Crymble, Kenneth Ross, and Samuel Smiles.

The very thorough investigation which was made by Henriques (*Ber.*, 1894, **27**, 2999) on the nature of the products resulting from the interaction of β-naphthol and sulphurating agents revealed the existence of two isomeric sulphides of β-naphthol. From the consideration of the data then available, Henriques concluded that these substances are probably stereoisomerides, and they have since been described as such in some of the larger works on stereochemistry. If this description is accurate, the type of stereoisomerism is clearly of a novel character; moreover, the acceptance of the hypothesis seems to carry with it certain fundamental assumptions with regard to the nature of the valencies in bivalent sulphur. Recently, however, facts have been observed which do not harmonise well with the hypothesis, and the experiments described in this paper were made with the desire to attain a more complete view of the evidence on either side.

Since the conclusion reached in this paper is adverse to the acceptance of these substances as stereoisomerides, it is necessary briefly to review the evidence which has been formerly adduced in favour of it. In the reaction of β-naphthol with the chlorides of sulphur or with sulphur in alkaline solution, Henriques (*loc. cit.*) obtained mixtures of substances, but in all cases the chief product was the α-sulphide of β-naphthol (m. p. 211°). The previous experience of Onufrowicz (*Ber.*, 1890, **23**, 3358) had shown that this substance may be oxidised by ammoniacal silver oxide, the so-called dehydro-β-naphthol sulphide being then formed by loss of two atoms of hydrogen. Besides improving on the method of preparing this substance, Henriques discussed its constitution, and concluded that it is a peroxide (I). It was further observed that reduction of the dehydro-compound with zinc dust and acetic acid did not yield the original sulphide, but an isomeric sulphide (m. p. 153°), which, however, was converted into the former by treatment with hot aqueous alkali hydroxide. These relations between the substances are shown by the following formulæ:



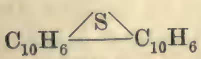
$$C_{10}H_6(OH)\cdot S\cdot C_{10}H_6(OH) \xrightarrow{O} C_{10}H_6<\overset{S}{O\cdot O}>C_{10}H_6 \xrightarrow{H_2} C_{10}H_6<\overset{S}{OH\quad HO}>C_{10}H_6$$

Stable, m. p. 211°. (I.) (II.) Unstable, m. p. 153°.

Henriques considered that the chemical identity of these substances was proved by the facts that they have the same molecular weight, and that they furnish isomeric diacetyl derivatives and lead salts of normal composition, and hence he turned to a hypothesis of stereoisomerism. It was assumed that the isomerism was due to the different relative positions of the naphthalene nuclei, the result being that in one substance the hydroxyl groups are adjacent to one another, and in the other more widely separated; in fact, the relationship postulated might have been summed up by applying the terms "*syn*" and "*anti*" to the two substances. Briefly speaking, the relationship was justified by the following facts:

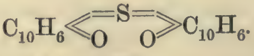
(1) The peroxide might be expected to yield the "*syn*"-compound (II, m. p. 153°) on reduction.

(2) This reduction-product when heated with sulphuric acid was easily dehydrated and, it may be observed, apparently reduced, yielding the dinaphthathiophen (III):



$$C_{10}H_6\overset{S}{—}C_{10}H_6$$

(III.)

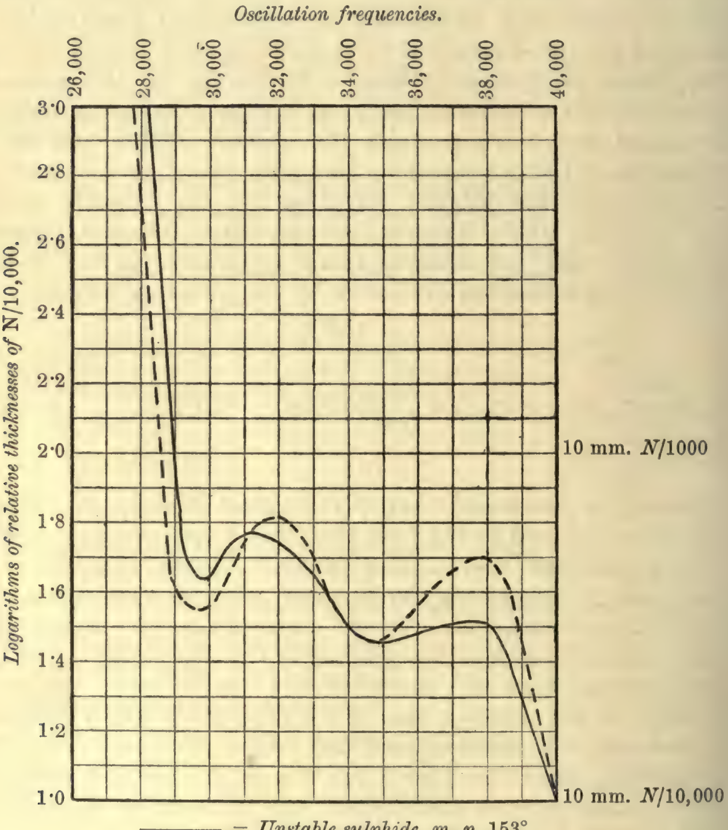


$$C_{10}H_6<\overset{=S=}{O\quad O}>C_{10}H_6.$$

(IV.)

(3) Dehydration of the supposed "*anti*"-isomeride (m. p. 211°) could not be effected, sulphuric acid yielding a tarry material.

In recent years other facts have accumulated which weaken the support given by these data; thus it has been shown that the "dehydro"-compound is a sulphonium-quinone (IV) (Trans., 1911, **99**, 976), and that it is possible easily to dehydrate the stable sulphide (Mauthner, *Ber.*, 1906, **39**, 1340; Christopher and Smiles, this vol., p. 710), good yields of the naphthathioxin being formed. Finally, it may be observed that the stable sulphide actually yields with sulphuric acid (Hilditch and Smiles, Trans., 1911, **99**, 415) small quantities of the naphthathioxin oxide; in fact, it is not at all surprising that naphthathioxin cannot be isolated from this interaction, for independent experiment shows that it is profoundly oxidised therein to an indefinite material.



——— = *Unstable sulphide, m. p.* 153°.
– – – = *Stable sulphide, m. p.* 211°.

The crucial test in favour of the hypothesis of stereoisomerism must lie in the demonstration that the two substances possess the requisite difference in reactivity towards dehydrating agents; but from the evidence available before the present work, all that can be said is that both substances may be dehydrated. Moreover, although the quinonoid formula for the "dehydro"-compound allows of the production of the required isomeride by reducing agents, the circumstance is not so clearly indicated as by the peroxidic formula. It is therefore clear that the somewhat slender basis of the hypothesis is so far reduced that the question of the relations between these substances must be entirely rediscussed.

It may be said at once that having repeated the determination of molecular weight of the sulphides and other quantitative experiments, we have at present no correction to make in the experimental data of Henriques.

The suggestion that these sulphides are polymorphously related may be at once dismissed, for the reactivity of their solutions is entirely different. Further evidence on this question has been obtained by the study of a physical property of their solutions; it will be seen on examining the adjacent figure that the absorption curves of the substances in alcohol are different in detail, although similar in general form, the stable sulphide having the characteristic bands more strongly developed than the unstable sulphide.

In the annexed table a summary is given of the various reactions in which these sulphides have been compared.

Reagent.	Result with stable sulphide.	Result with unstable sulphide.
H_2SO_4	Cold reagent: naphthathioxin oxide	Hot reagent: naphthathiophen.
$POCl_3$ (under same conditions)	20 per cent. naphthathioxin	2 per cent. naphthathiophen.
KOH, aq.	Hot reagent: stable	Cold reagent: part resinified and part converted into stable sulphide.
Ph·N:NOH in alkaline solution	Benzeneazo-β-naphthol	Colourless, unstable additive (?) product.
$FeCl_3$ in alcohol	Green colour	Yellow.

EXPERIMENTAL.

Interaction with Sulphuric Acid.—The behaviour of the stable sulphide with this reagent has been described elsewhere. With cold sulphuric acid very small yields of naphthathioxin oxide are obtained (Hilditch and Smiles, Trans., 1911, **99**, 415), whilst the hot reagent yields tarry material, from which no definite product could be isolated (Henriques, *loc. cit.*). With the unstable sulphide the experimental plan of Henriques (*loc. cit.*) was followed, and his results were confirmed, although the yields of naphthathiophen obtained were not so high as that mentioned by this author.

Interaction with Phosphoryl Chloride.—This reagent afforded an opportunity of studying the dehydration of the isomerides under identical conditions, which were as follows: Ten grams of the sulphide and an equal weight of phosphoryl chloride were dissolved in 170 c.c. of hot tetrachloroethane, and the mixture was maintained at 107—110° for four hours. Subsequently the solvent was removed by a current of steam, and the residue was extracted with cold aqueous alkali hydroxide. The insoluble portion was then isolated by filtration. In the case of the unstable sulphide this operation must be very rapidly effected, for the alkaline reagent resinifies a portion of the unchanged sulphide. With either sulphide the products were almost pure, the experiment with the stable sulphide giving 2 grams of naphthathioxin, and that with the unstable yielding 0·2 gram of naphthathiophen. After recrystallisation these substances were identified by the melting point taken alone or admixed with samples of these substances obtained from other sources. The naphthathioxin melted at 166°, and the naphthathiophen at 146—147°.

Attention may be here drawn to the apparently peculiar nature of the reaction which takes place when the unstable sulphide is treated with these dehydrating agents. It is difficult to obtain direct proof of the thiophen-structure which has been assigned to the product by Henriques, but in future experiments it is hoped that the synthesis may be effected. The stated constitution has been provisionally accepted.

Interaction with Aqueous Alkali Hydroxide.—Both sulphides are readily soluble in the cold reagent. The solution of the compound of higher melting point is stable, and very little change can be detected in it, even after exposure to the air for some weeks; on the other hand, the cold alkaline solution of the unstable sulphide rapidly becomes turbid on being kept, a resinous material being deposited, whether air is excluded or not from the vessel and in presence of a reducing agent such as sodium hyposulphite. After the lapse of twenty-four hours the resinous material was removed, and, on acidifying the filtrate, the stable sulphide was obtained and identified in the usual manner. It is thus evident that the unstable sulphide is partly decomposed by this reagent and partly transformed into the stable. Henriques (*loc. cit.*) has previously recorded this conversion by the boiling reagent, but apparently did not observe the decomposition which simultaneously occurs. It may be here observed that the unstable sulphide partly decomposes if treated with boiling organic solvents, but in the cases examined conversion did not take place.

Interaction with Diazobenzene.—Henriques (*loc. cit.*) has stated that, when treated in alkaline solution with sodium diazobenzenesulphonate, both sulphides yield the corresponding derivative of benzeneazo-β-naphthol, the sole difference between the two being that the unstable combines more slowly than the stable sulphide, which reacts instantaneously. Experimental details were not given. We have repeated these experiments, using diazobenzene, and are unable to confirm this result with the unstable sulphide. The conditions adopted were as follows:

Two molecular proportions of benzenediazonium chloride were added to an ice-cold solution of the naphthol sulphide in excess of aqueous alkali hydroxide.

The solution of the stable sulphide at once interacted, yielding a dark red precipitate, which finally set to a brittle mass. This was repeatedly recrystallised from alcohol, when benzeneazo-β-naphthol was obtained. The substance was identified by means of the mixed melting-point (131°) method, and by conversion into the monobromo-derivative by Hewitt and Auld's method (Trans., 1902, **81**, 1202), the product (m. p. 169—170°) being again identified by comparison with the monobromo-derivative prepared from another sample of benzeneazo-β-naphthol.

The solution of the unstable sulphide when mixed with the diazonium salt immediately yielded a cream-coloured, flocculent precipitate, no evolution of gas or other decomposition being observed as with the stable compound. Attempts to isolate this substance for purification were not successful, for when collected, even in an ice-cold condition, it rapidly decomposed with evolution of gas, forming an orange mass. Repeated attempts to isolate benzeneazo-β-naphthol from the latter product were unsuccessful.

The colour reactions with ferric chloride require no further comment than the remark that the normal sulphide behaves in this respect similarly to β-naphthol.

Of all these comparative experiments those conducted with dehydrating agents have the most direct bearing on the hypothesis of stereoisomerism. It is clear from the stated results that, even if the hypothesis is tenable, the postulated relationship between the sulphides must be reversed, since the experiment with phosphoryl chloride shows that the stable or supposed "*anti*"-sulphide is dehydrated much more readily than the unstable or "*syn*"-compound.

There is, however, no need further to discuss this question, for, on taking a general review of the results, it becomes evident that the chemical nature of these sulphides is entirely different, and the difference, not being merely of degree in reactivity, is not such as can be satisfactorily explained by any hypothesis of stereoisomerism.

The contrast is most distinctly seen in the reaction with sulphuric acid, in which the stable sulphide is dehydrated and oxidised, whilst the unstable suffers dehydration and apparently reduction.

Whilst thus discarding the hypothesis of stereoisomerism, more cannot at present be said of the relationship between these compounds than that the stable sulphide behaves as a true derivative of β-naphthol, whilst the unstable does not. Experiments are now in progress which further emphasise this distinction between them, and it is hoped that the results will elucidate the relationship. It is, however, evident that the difference between the two sulphides must lie either in the naphthalene system or in the situation of the thio- and hydroxyl groups, or in the structural form of the latter.

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CXXI.—*The Oxidation of Atmospheric Nitrogen in Presence of Ozone.*

By **Thomas Martin Lowry.**

Some five years ago the writer had the opportunity of making a spectroscopic examination of the bleaching gases produced by passing air (*a*) through an ozoniser, (*b*) through a series of spark-gaps, (*c*) through both ozoniser and spark-gaps, either in parallel or in series, in accordance with a process devised by Leetham in 1903. The experiments showed that the superior bleaching properties of the Leetham gas might be attributed in part to an increased yield of nitrogen peroxide, which appeared to be produced as a result of the oxidation by ozone of an unstable, oxidisable variety of nitrogen manufactured in the spark-gaps.

Electrical Arrangements.—In normal working, air from a Root's blower was sent at the rate of about 70 cubic feet per minute through an Andreoli ozoniser, containing thirteen aluminium sheets or grids, 30″ × 30″ in area, separated by sheets of micanite; it then passed into a rectangular box containing six pairs of iron studs, separated to a distance of 3/32″, three of which were employed as spark-gaps. The spark-gaps and ozoniser were all in series, the whole system taking an alternating current of 0·1 ampere at 9000 volts. Arrangements were available whereby the ozoniser and spark-gaps could act on the air, either consecutively or in parallel; it was also possible to employ two ozonisers or to increase the number of spark-gaps to seventeen.

Spectroscopic Arrangements.—As the gases to be examined were very dilute, it was necessary to use an exceptionally long column in order to observe the absorption-spectrum of the gas. The experiments were therefore made with a wooden trunk, 64 feet in length and 3″ × 3″ in internal section, the volume of the trunk being thus about 4 cubic feet. The gas from the ozoniser or spark-box was led into the trunk at one end through a distribution-box and lead piping, the total volume of which was probably less than that of the trunk. The trunk was provided with glass windows at each end; at the near end, a condensing lens of 3¼″ focal length was illuminated by means of a Nernst lamp with filament vertical; at the far end, the light was concentrated by an achromatic lens of 11″ focal length on the slit of a spectroscope. On account of the great distance between the two lenses the effective illumination was confined to that emanating from a small portion of the centre of the filament, about 1/100″ in diameter, and the image on the slit was always circular.

The spectroscope was provided with a single glass prism; the collimator lens was of 13″ focus, and the camera lens of 22″ focus. An exposure of six minutes with Wratten and Wainwright's "Panchromatic" plates was found to be sufficient when two minutes were allowed for development in total darkness.

Standard Spectra of Nitrogen Peroxide.—Standard mixtures of nitrogen peroxide and air were made by passing nitric oxide (prepared from mercury and nitric acid and tested by absorbing a sample with ferrous sulphate solution) at a known rate through a capillary tube into the centre of an air-jet. The flow of oxide was determined by the displacement of the gas by means of mercury from a large cylinder-funnel of 1 litre capacity; the mercury was passed in at a regular rate through a small funnel drawn out into a capillary tube; from the total volume of mercury used and the time occupied by the experiment, the average rate of flow was calculated. The flow of air was regulated by means of blow-off taps, and was measured by means of a standard meter. The consistency of the results obtained showed that this method of working was sufficiently accurate. The standard mixtures prepared in this way were passed into the 64-foot trunk, and their absorption spectra were observed and photographed again and again until it was easy to judge the concentration of the gas by mere inspection, even without referring to the negatives which formed the permanent record of the experiments.

Visibility of Nitrogen Peroxide.—No absorption could be detected by the eye or in the photographs when using a 64-foot column of air charged with 1/16,000 and 1/12,000 parts by volume of nitrogen peroxide. The absorption spectrum began to be visible in a 64-foot column at a concentration of about 1/8000 NO_2; when using a 15-foot column * it could just be seen at 1/3500 concentration. The visibility of the spectrum was therefore roughly proportional only to the square-root of the length of the column of gas, when all the other experimental conditions remained unchanged.†

At higher concentrations the absorption became very marked; at a concentration of 1/3500 the spectrum showed, throughout the greater part of its length, the ripples or flutings characteristic of nitrogen peroxide; at 1/1700 about half the spectrum was blocked out; and at 1/1200 about two-thirds had disappeared, the remainder showing very strong bands or flutings.

Action of the Ozoniser and of the Spark Discharges on Air.

On passing into the 64-foot trunk air which had been submitted to the action of the ozoniser or of three spark-gaps, no trace of nitrogen peroxide could be detected, either by the eye or in photographs of the absorption spectra; but the Leetham gas, which had been submitted to both forms of spark discharge by passing through the ozoniser and then through three spark-gaps, gave a well-marked spectrum, agreeing closely with that of nitrogen peroxide at a concentration of about 1/4000 NO_2. This remarkable development of the spectrum of nitrogen peroxide is in accord with the fact (to which Cramp and Hoyle have called attention, *Proc. Inst. El. Eng.*, 1909, **42**, 328) that the yield of this gas from an arc-discharge can be increased considerably by ozonising the air-supply.

Comparison of the Three Varieties of "Combined" Gas.—Contrary to what was expected, an absorption spectrum of almost equal intensity was produced when the direction of the air-current was reversed, so that the gas passed through the spark-gaps and then through the ozoniser. Under these conditions the ozoniser was converted into an efficient generator of nitrogen peroxide. This novel function of the ozoniser is the more remarkable because ready-made nitrogen peroxide was completely bleached by passing slowly through the machine, probably because it was oxidised to nitric anhydride or nitric acid (compare Helbig, *Atti R. Accad. Lincei*, 1903, [v], **12**, 211); the spectrum could be restored completely by passing the gas through a hot tube, an operation that had no effect whatever on the spectrum of the gas prepared by the Leetham process.

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* A glass slide was inserted so that the gas only entered the first portion of the trunk and then escaped into the atmosphere.

† An even more marked diminution of visibility by dilution is seen on comparing the present observations with those of Robertson and Napper (Trans., 1907, **91**, 761), who were able to detect a concentration of 1/2000 NO_2 in a tube 40 cm. in length.

The problem of discovering the nature of the mechanism whereby these increased yields of nitrogen peroxide were produced was much simplified when it was found that an absorption spectrum of only slightly less intensity could be produced by running the two air-currents in parallel and mixing the gases from the two machines before observing their absorption spectra. It was then evident that the increased production of peroxide was not an electrical phenomenon, but was due to a purely chemical interaction between the ozone and some oxidisable form of nitrogen manufactured in the spark-gaps.

Action of Seventeen Spark-gaps on Air.—As the high-tension discharge without a solid dielectric is used to manufacture nitrogen peroxide on a large scale in commercial practice, experiments were made to detect this gas in air which had been submitted more strongly to this form of discharge. For this purpose the whole of the power available was used to energise a series of seventeen spark-gaps. The product, when passed quickly through the trunk, showed a very weak spectrum of nitrogen peroxide, the concentration being perhaps 1/7000; a stronger spectrum, corresponding with a concentration of about 1/3000 NO_2, was observed when the same gas was passed through the trunk at the rate of only half a cubic foot per minute, in order to allow ample time for the gas to mature. No such increase of intensity was observed in the gases prepared with the help of ozone. The increase in the case of the gas from the seventeen spark-gaps may be taken to indicate that the production of nitrogen peroxide by this form of discharge is not a direct or instantaneous process, but that the peroxide is formed gradually during a period slightly longer than the time (about seven seconds) required to drive the gas at full speed through the trunk.

The Slow Oxidation of Nitric Oxide.—As it is well known that nitric oxide is oxidised only slowly by oxygen (Raschig, *Zeitsch. angew. Chem.*, 1905, **18**, 1281), but very quickly by ozone (Strutt, *Proc. Roy. Soc.*, 1911, *A*, **85**, 533), it was conceivable that the main action of the ozone in the Leetham process was to accelerate the oxidation of nitric oxide. If this had been the explanation of the phenomena, however, spectra of equal intensity should have been produced by merely allowing a longer time for the gas from the three spark-gaps to mature before observing its absorption spectrum, whilst the seventeen spark-gaps should, under similar conditions, have given a yield of nitrogen peroxide five or six times greater than that produced by three spark-gaps with the help of ozone; actually, however, the seventeen spark-gaps gave a yield only about 30 per cent. greater, or about the same yield as that which might have been expected from four spark-gaps with the help of ozone. The inefficiency of the later spark-gaps in producing oxides of nitrogen might be attributed in part to the higher temperature of the air supplied to them, or even to some destruction of nitrogen peroxide already formed in the earlier spark-gaps; but no explanation of this kind would be adequate to account for some thirteen additional spark-gaps doing nothing whatever to increase the yield of nitrogen peroxide beyond that already available, with the help of ozone, from the first four.

An Oxidisable Variety of Nitrogen.

In view of the facts described above, the idea that the ozone acted merely as a rapid oxidiser of nitric oxide was abandoned, and the view was adopted that the oxidisable substance was a modification of nitrogen itself. This opinion was expressed as follows: "It seems to be clearly demonstrated by the experiments of Carius and Berthelot that ordinary nitrogen is not oxidised by ozone, but the present observations show that, when air has been sparked, the nitrogen, probably because it has become 'atomised' ($N_2 \longrightarrow 2N$), 'electrified,' or 'ionised' (that is, conducting), is readily oxidised by ozone. The ordinary 'combined' arrangement generates 'ionised nitrogen' in air that is already ozonised; the reversed arrangement leads 'ionised nitrogen' into an apparatus which produces ozone; and finally, in the parallel arrangement 'ionised nitrogen' and ozone are produced separately and merely mixed together. The ozoniser is able to decompose oxygen and convert it into ozone, but the discharge is not sufficiently powerful to break up many of the more stable nitrogen molecules, and the product is therefore mainly ozone. The spark discharge, on the other hand, probably decomposes both the oxygen and the nitrogen molecules; but owing to the relatively small amount of ozone that is formed (and the relative inertness of the ozone at high dilutions), only a part of the 'ionised' or 'atomised' nitrogen becomes oxidised, and most of it merely reverts to molecular nitrogen. The more quickly the 'ionised' nitrogen can be brought into contact with ozone the smaller will be the proportion that thus reverts, and the greater will be the yield of nitrogen peroxide; in this way it is easy to account, not only for the production of nitrogen peroxide by the three modifications of the Leetham process, but also for the relative quantities produced in the three cases."

At the time when these observations were made, the conclusion that nitrogen could be rendered active by a spark-discharge was so far novel that it did not appear to be desirable to put it forward on the basis of a single series of experiments. The recent experiments of Strutt (*Proc. Roy. Soc.*, 1911, *A*, **85**, 219; 1911, *A*, **86**, 56; 1912, *A*, **86**, 105), however, have established so definitely the existence of a chemically active variety of nitrogen, that no hesitation need now be felt in assuming that a similar substance may be produced by the electrical discharge under conditions differing somewhat widely from those used in the experiments of Strutt. The behaviour of the two products is, however, not the same. I am indebted to Prof. Strutt for the information that when chemically active nitrogen and ozonised oxygen are mixed together at a low pressure and then cooled with liquid air, no trace of oxides of nitrogen can be detected in the product. Whether this difference of behaviour is due to some difference in the nature of the oxidisable substance produced by sparking air under ordinary pressures, or whether it is due merely to the different experimental conditions, is a matter that cannot be decided by means of the data at present available. But the observations now described serve at least to suggest the possibility that an active variety of nitrogen may be produced by the electric discharge in air under ordinary pressures, and that the formation of such a substance and its oxidation by ozone may play an important part in technical processes for the fixation of nitrogen. It is in order to call attention to this possibility, rather than with the idea of giving any dogmatic explanation of the experiments, that the present paper has been written.

The view that nitrogen is broken up by the spark-discharge and converted into an unstable oxidisable modification, affords a simple and adequate explanation of the remarkable effects produced by combining the "spark" and the "silent" discharges in the way suggested by Mr. Leetham. It only remains to suggest some allied phenomena to which the hypothesis of oxidisable nitrogen may be applied. Foremost amongst these is the production of nitrogen peroxide by the spark discharge without the addition of ozone. The simultaneous production of oxides of nitrogen and of ozone by the discharge is so familiar (see, for instance, Cramp and Hoyle, *Proc. Inst. El. Eng.*, 1909, **42**, 312; Strutt, *Proc.*

Roy. Soc., 1911, *A*, **85**, 536) that no objection can well be taken to the idea that *the spark-discharge may give rise both to active nitrogen and to ozone*, the proportions varying very widely with the experimental conditions. In the experiments now described there must have been a marked deficiency of ozone in the gas from the spark-gaps, since added ozone was capable of producing a very large increase in the yield of nitrogen peroxide; but under other conditions ozone is the predominant product. There can be no doubt that by a happy combination of conditions, oxidisable nitrogen and ozone might be produced by the spark-discharge in just the right proportions to give a maximum yield of nitrogen peroxide with no excess of either active constituent.

The slow maturing of the gas from the spark-gap may also be explained on the same hypothesis, as due, not necessarily to the slow oxidation of nitric oxide by air, but (on an equally reasonable view) to the slow oxidation of active nitrogen by ozone at extreme dilutions.

Finally, it is not unreasonable to ask whether the production of oxides of nitrogen by the electric discharge in all its various forms must not be attributed to the interaction of active nitrogen and active oxygen, either in the form of ozone or of atomic oxygen. If so, the production and oxidation of active nitrogen must already be ranked amongst the foremost of the technical operations of the present day.

The author is indebted to Mr. Henry Simon, of Manchester, for permission to publish an account of the experiments now described, to Mr. Cramp for much helpful criticism, and to Prof. Strutt for permission to refer to his unpublished experiments on the admixture of ozone and chemically active nitrogen. To each of these the author wishes to accord his heartiest thanks.

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CXXII.—*The Mechanism of the Racemisation of Some Hydroxy-acids by Heat.*

By Dan Ivor James and Humphrey Owen Jones.

The work described in this paper is a part of a more general investigation into the process of racemisation which was begun with the idea of trying to elucidate the mechanism of the process, and in particular to determine whether the interesting hypothesis put forward by Werner ("Handbuch der Stereochemie") is necessary to explain the process or whether racemisation does not, in all cases, take place through the formation of an intermediate inactive compound.

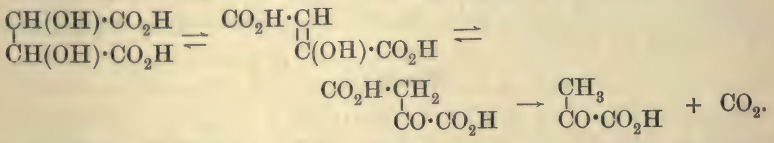
The experiments here described were begun with malic acid in aqueous solution, and have been extended to tartaric acid.

Aqueous solutions of malic acid when heated to 165—170° become inactive in about ten days. It was soon found that accurate determinations of the rate of change were not possible in glass tubes, even when the hardest glass was used, as the tubes behaved in an erratic manner, due probably to substances dissolved out of the glass.

It was soon found that in the solutions of malic acid used (concentration 8—10 per cent.), fumaric acid was formed and separated from the solution on cooling. As the conversion of fumaric acid into malic acid on heating in aqueous solution is well known, it follows that the change is reversible, but so far we have not been able to get exactly the same state of equilibrium established starting from either malic or fumaric acid. A study of the curves showing the rate of change of malic acid into fumaric and the rate of racemisation of malic acid make it very probable that the racemisation of malic acid in aqueous solution takes place through the intermediate formation of the inactive fumaric acid.

The rate of racemisation of sodium malate was found to be very much slower than that of malic acid, and fumaric acid was not formed in this case, at any rate, in sufficient quantity to be detected. In presence of excess of a base like pyridine, the process of racemisation was more rapid than with malic acid alone. No fumaric acid could be detected, and it therefore seems probable that the mechanism of the process in the two cases is different.

It seemed possible that a change of the same type might take place during the racemisation of tartaric acid, in which case the intermediate product would be hydroxyfumaric acid or oxalacetic acid. This should decompose partly into pyruvic acid and carbon dioxide, so that the following changes might be expected:



$$\begin{array}{l}\mathrm{CH(OH)\cdot CO_2H}\\ \mathrm{CH(OH)\cdot CO_2H}\end{array} \rightleftharpoons \begin{array}{l}\mathrm{CO_2H\cdot CH}\\ \qquad\ \ \mathrm{C(OH)\cdot CO_2H}\end{array} \rightleftharpoons \begin{array}{l}\mathrm{CO_2H\cdot CH_2}\\ \qquad\ \ \mathrm{CO\cdot CO_2H}\end{array} \longrightarrow \begin{array}{l}\mathrm{CH_3}\\ \mathrm{CO\cdot CO_2H}\end{array} + \mathrm{CO_2}.$$

It was found that on heating solutions of tartaric acid, carbon dioxide was produced in increasing quantities, and the presence of pyruvic acid in the solution was established.

Method of Experiment.—Solutions containing 8—10 per cent. of malic acid were sealed up in tubes of hard combustion glass, each containing about 10 c.c., and heated in an oil-bath at a constant temperature of about 165°, which could be maintained within 1°. When the tubes had reached the temperature of the bath, one was removed, its rotatory power determined and this was taken as the arbitrary zero for the experiment. As the rotatory power of malic acid is so small, the solution was always mixed with ammonium molybdate in quantity sufficient to increase the observed rotation to a maximum. This result is attained when one molecular proportion of ammonium molybdate is added for every two of malic acid. The use of ammonium molybdate in this proportion has the further advantage that the curve connecting the increase of rotation of the malic acid with the relative proportions of acid and molybdate is fairly flat in this region, so that small changes in the amount of malic acid present due to decomposition by heat would not affect to any appreciable extent the increase in the rotation caused by the addition of molybdate.

The rotations were measured usually in a 2-dcm. tube at 15°.

Two experiments may be selected to show the kind of result obtained in this way:

I. Temperature of bath, 158·5°.

9·514 Grams of malic acid in 100 c.c. After heating, 10 c.c. of this solution were mixed with 10 c.c. of an ammonium molybdate solution containing 43·9 grams of salt in 100 c.c. of solution.

The first column gives the number of hours for which the tube had been heated; the second column gives the observed rotation, and the third gives the velocity constant of the reaction calculated from the equation for a reaction of the first order.

TABLE I.

Hours.	α_D.	*K*.	Hours.	α_D.	*K*.
0	+73·66°	—	9	+68·80°	0·00329
3	71·20	0·004917	12	67·70	0·00310
6	70·11	0·003276			

II. Temperature 170°.

9·43 Grams of malic acid in 100 c.c. Ammonium molybdate, 43·4 grams in 100 c.c.

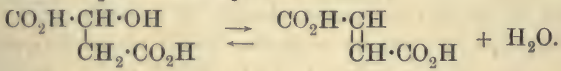
TABLE II.

Hours.	α_D.	*K*.	Hours.	α_D.	*K*.
0	+68·09°	—	50	+32·65°	0·0063
5	64·29	0·0050	74	47·25	0·00215
11	56·74	0·0072	101	11·42	0·0077
22	51·93	0·0053	124	23·25	0·00376
34	50·51	0·0040			

It is evident from the behaviour of the last four tubes that the velocity of the change is erratic, and is influenced by variable conditions, possibly substances dissolved out of the glass, and thus it is not possible to obtain a velocity constant, but it would appear that the temperature-coefficient of the reaction is not large. These conclusions are supported by the same observations in every set of experiments made.

In these experiments it was observed that in the tubes which had been heated for more than forty hours a white, crystalline deposit had formed, and the quantity of this deposit was clearly increased by longer heating. This substance was identified as fumaric acid. The formation of fumaric acid in a 10 per cent. solution of malic acid was unexpected, but it is well known that fumaric acid is converted into malic acid by heating with water to 170°.

It follows, therefore, that an equilibrium must be established in the solution represented by the scheme:



$$\begin{array}{l} \mathrm{CO_2H\cdot CH\cdot OH} \\ \qquad\mathrm{CH_2\cdot CO_2H} \end{array} \rightleftarrows \begin{array}{l} \mathrm{CO_2H\cdot CH} \\ \qquad\mathrm{CH\cdot CO_2H} \end{array} + \mathrm{H_2O}.$$

This reversible change was therefore examined quantitatively. We were not able to devise a satisfactory direct method of estimating the amount of fumaric acid formed in the presence of malic acid, so the amount of fumaric acid which had been formed was ascertained by titrating the residual solution after keeping to allow of the separation of fumaric acid.

The solubility of fumaric acid at 12° was found to be 0·0035, that is, 1 gram in 286 c.c. of water, and this was not altered appreciably by the presence of malic acid at the concentrations used. The solutions of malic acid of known strength were therefore heated in tubes as already described, the tubes removed from the bath from time to time were cooled, allowed to remain for some time, and shaken vigorously at intervals to prevent the solution remaining supersaturated with fumaric acid. Five c.c. of the solution were then titrated with *N*/5-potassium hydroxide.

One such experiment will serve to illustrate the kind of result obtained: malic acid, 8·844 grams per 100 c.c. Temperature 162°.

Column I gives the number of hours the tube was heated; column II gives the number of c.c. of *N*/5-potassium hydroxide required to neutralise 5 c.c. of solution; column III gives the percentage of malic acid present calculated from the titre after subtracting the titre corresponding with 5 c.c. of a saturated solution of fumaric acid, that is, 1·5 c.c. of *N*/5-potassium hydroxide; and column IV gives the rotation of the solution determined in a 1-dcm. tube after dilution and mixing with ammonium molybdate.

TABLE III.

I.	II.	III.	IV.
0	33·0	100·0	+14·80°
24	32·5	94·0	13·26
48	30·2	87·0	11·33
72	29·2	84·0	8·01
120	28·9	83·0	7·78
144	29·4	84·5	7·35
168	29·6	85·1	6·94
192	29·2	83·9	6·14

The values in the second and third columns show clearly that there is no further change of malic into fumaric acid after the tubes have been heated for about three days. The equilibrium state would therefore appear to be established when the solution contains about 84 per cent. of the original quantity of malic acid, or when the ratio of molecules of malic to molecule of fumaric acid is about 5·3:1.

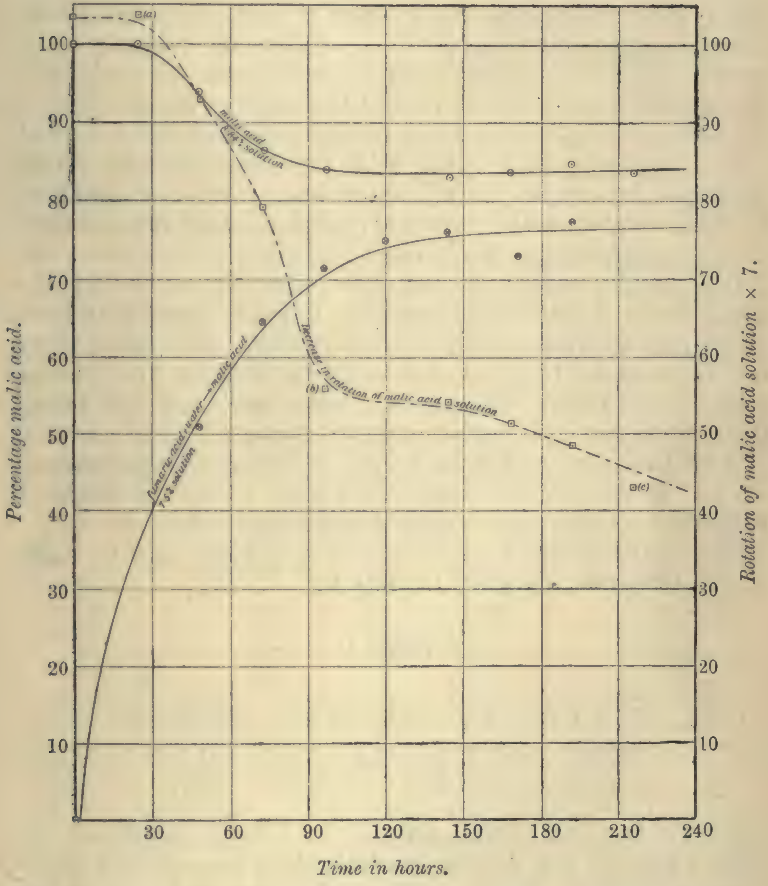
In order to study the reverse change of fumaric acid into malic acid on heating in aqueous solution, small weighed quantities of fumaric acid were introduced into sealed tubes, together with the quantity of water required to make all the solutions in one set of tubes up to the same concentration when the tubes were heated and the fumaric acid had dissolved. The tubes were then heated to a constant temperature; at intervals of twenty-four hours a tube was removed, allowed to remain with occasional shaking to allow the fumaric acid to separate completely from its supersaturated solution. Five c.c. of the solution was then titrated with $N/5$- or $N/10$-potassium hydroxide solution. Several series of experiments were made, in which the period of heating was extended to one hundred and ninety-two hours at 162—163°, and the last tube removed was kept for three weeks at 25° before being titrated. The results of one of these series only will be given here (table IV).

TABLE IV.

Hours.	Fumaric acid, grams.	Water added, c.c.	No. of c.c. of $N/5$-KOH required for 5 c.c. of solution after filtering from the fumaric acid and then subtracting 2·45 c.c. for solubility of fumaric acid.	Fumaric acid changed, per cent.
24	0·785	10·35	13·65	41·7
48	0·979	13·0	18·18	56·0
72	0·907	12·0	21·0	64·5
96	0·778	10·3	23·55	72·3
120	0·766	10·12	24·35	74·8
144	1·01	13·45	24·65	76·1
168	0·863	11·4	23·8	73·0
192	0·950	12·55	24·9	76·3

The volume of $N/5$-potassium hydroxide required by 5 c.c. of a saturated solution at 25° is 2·45 c.c.

It will be seen from the figures in columns 4 and 5 that the state of equilibrium is reached after about four days' heating, but that the final state of equilibrium is reached when only about 75 per cent. of fumaric acid has been changed, whereas in the change of malic acid there was 84 per cent. of this left when equilibrium was reached.



The reason of this discrepancy has not yet been found, but the problem will be further examined.

The bearing of this reversible change on the mechanism of the process of racemisation of malic acid is interesting, and is very clearly indicated when the curve of the rate of formation of fumaric acid is compared with the curve for the rate of racemisation of malic acid (see diagram). These curves are plotted from the results given in tables III and IV.

The latter curve seems to consist of two separate portions, (*a*) to (*b*) and (*b*) to (*c*); the former represents the relatively rapid racemisation of malic acid by conversion into fumaric acid. This portion coincides as regards duration with that part of the curve above which represents the change of malic into fumaric acid preceding the establishment of an equilibrium condition. The portion (*b*) to (*c*) represents the slower process of racemisation which takes place when the rate of formation of fumaric acid has reached a minimum after the equilibrium state has been reached.

This indicates that malic acid racemises primarily through conversion into fumaric acid, so that when a state of equilibrium has been reached in the reversible change the rate of racemisation should be reduced to a much smaller value.

It is usually stated that although malic acid on heating alone loses water, the sodium salt does not. It was of interest, therefore, to compare the rates of racemisation of malic acid and its sodium salt in solutions by equivalent concentrations of 8·01 per cent. acid. The addition of ammonium molybdate does not increase the rotatory power of sodium malate; consequently, 10 c.c. of the salt solution were added to 10 c.c. of *N*-hydrochloric acid, and 10 c.c. of the mixture were mixed with 10 c.c. of ammonium molybdate solution and examined in a 2-dcm. tube.

The results obtained with solution of the acid and its sodium salt at 168—169° are given in table V.

TABLE V.

Hours.	α_D for sodium salt.	α_D for acid.	Hours.	α_D for sodium salt.	α_D for acid.
0	+25·03°	+50·55°	48	+23·14°	+39·15°
6	23·59	45·42	54	22·76	34·82
44	23·90	42·05	68	22·17	29·45

In the tube containing sodium salt, small amounts of silica were deposited, but no charring took place, nor was any pressure developed and no fumaric acid could be detected. No charring took place, nor did pressure develop in any of the tubes containing free acid.

It is clear that the rate of racemisation of the sodium salt is very much smaller than that of the free acid, and this is probably due to the fact that little or no fumaric acid is formed from the sodium salt.

As the process of racemisation is in many cases greatly accelerated by alkali, as, for instance, in the case of mandelic acid, some sodium malate solution was mixed with a half equivalent of alkali and heated to 120°. Unfortunately, the glass of the tube was attacked, and the solution had to be filtered from the white, flocculent precipitate. The solutions were acidified and mixed with ammonium molybdate as usual.

TABLE VI.

Hours.	Rotation.
0	+17·71°
17	15·0
24	14·59
48	+15·4°
72	10·92
120	14·16

It is clear that alkali accelerates the racemisation very considerably, but it is probable that the mechanism of the process is entirely different under these conditions.

As concordant results could not be expected in this case owing to the variable action of the alkali on the glass, an attempt was made to study the influence of pyridine on the rate of racemisation of malic acid. In the experiment quoted below (table VII) the molecular proportions of acid to pyridine were 1 to 3. Ammonium molybdate was added to the solution without the previous addition of hydrochloric acid, as this invariably caused the precipitation of molybdic acid. The bath was heated to 150°.

TABLE VII.

Hours.	α_D in 10-cm. tube at 14°.
0	+7·41°
18	5·18
24	5·52
48	3·32
72	+2·51°
120	3·44
144	1·60
168	0·68

As the heating continued the solutions acquired a brown colour, and considerable pressure was developed; the colour, however, did not interfere with the determination of the rotatory power.

No velocity constant can be calculated from the above results, and, as decomposition occurs to an appreciable extent, the results are not comparable with those obtained with the free acid and its sodium salt; but it is clear that racemisation takes place rapidly under these conditions.

Experiments with Tartaric Acid.

As explained in the introduction, the fact that the racemisation of malic acid by heat appears to take place through the formation of fumaric acid, it seemed probable that the racemisation of other hydroxy-acids might take place through a similar intermediate stage, which in the case of tartaric acid would be hydroxyfumaric acid. This view was suggested by Nef (*Annalen*, 1904, **335**, 191) to explain the formation of racemic and mesotartaric acids by the action of heat on tartaric acid. The possibility that hydroxyfumaric acid or its isomeride oxalacetic acid would lose carbon dioxide and yield pyruvic acid, seems to have been overlooked. To ascertain if this took place, some tartaric acid solution was heated to 175° in sealed tubes, which were opened, boiled to remove carbon dioxide and titrated at intervals.

TABLE VIII.

Hours.	No. of c.c. of NaOH required by 5 c.c.	Decomposition of the acid, per cent.
0	23·05	0·0
24	20·5	22·2
48	17·6	47·3
72	17·05	55·9
96	16·4	57·7

The solution acquired only a pale straw colour, which is not in accordance with the observations of Holleman (*Rec. trav. chim.*, 1898, **17**, 66), who states that the solutions became brown, and had to be cleared by treatment with charcoal. Holleman observed that considerable pressure was developed in the tubes, but did not draw the conclusion indicated above.

The solutions of tartaric acid after heating had the odour of pyruvic acid, and from them pyruvic acid hydrazone was isolated and identified by its melting point (191°).

It was shown above that the sodium salt of malic acid racemises very slowly, and accordingly tubes containing solutions of *N*-sodium tartrate were heated to 175° and examined at intervals. The solutions were all found to be alkaline, and the amount of decomposition was estimated by adding 5 c.c. to 20 c.c. of *N*/10-sulphuric acid, boiling to expel carbon dioxide, and then titrating the residual acid with *N*/10-sodium hydroxide. The rotation of the solutions was also determined.

TABLE IX.

Hours.	α_D in 1-dcm. tube at 14°.	No. of c.c. of *N*/10-NaOH required.	Decomposition of tartrate, per cent. (calculated).
0	+6·37°	20·0	0·0
24	6·14	17·75	4·50
72	5·46	17·60	4·80
96	2·73	12·55	14·90
120	1·28	8·4	23·20

The glass was attacked to a considerable extent in the tube which had been heated for a long time, and the solutions in these tubes had acquired a light brown colour.

It will be observed that the rate of racemisation and of decomposition appears to be more rapid after seventy-two hours' heating than before this time. This is probably to be attributed to the liberation of alkali owing to the formation of pyruvic acid and catalysis of the change by this. Böeseken (*Rec. trav. chim.*, 1898, **17**, 224) has shown that alkali accelerates the process of racemisation by heat, but he found that the solutions acquired a deep colour.

These observations are being extended to other active hydroxy-acids, and preliminary experiments with lactic and mandelic acids seem to show that racemisation in these cases takes place through the intermediate stage of formic acid and an aldehyde.

The expenses of the work have been partly defrayed by means of grants from the Government Grant Committee of the Royal Society, for which we are glad to make this acknowledgment.

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CXXIII.—*The Dynamic Isomerism of Ammonium Thiocyanate and Thiocarbamide.*

By WILLIAM RINGROSE GELSTON ATKINS, and EMIL ALPHONSE WERNER.

THE transformation of ammonium thiocyanate into thiocarbamide and vice versa at a temperature of 170—180° was shown a few years ago to be a reversible change, in which a condition of dynamic equilibrium occurs when the components are present in the proportions of 25 per cent. of thiocarbamide and 75 per cent. of ammonium thiocyanate (Emerson Reynolds and Werner, Trans., 1903, **83**, 1). Equilibrium is reached in thirty minutes at 180°, in forty-five minutes at 170°, and is not sensibly altered by prolonging the time.

The eutectic point of the "equilibrium mixture" was shown to be about 105°.

Whilst it was not possible to extract by solvents from the fused material any definite compound corresponding with the composition of the equilibrium mixture, it was suggested by Emerson Reynolds and Werner (*loc. cit.*) that the particular equilibrium proportion results from the formation in the fusion of the compound $CSN_2H_4(NH_4SCN)_3$, sufficiently stable at 170—180° to prevent the further transformation of either isomeride. This explanation appeared to throw some light on the cause of the relatively poor yield of thiocarbamide from ammonium thiocyanate, as compared with the similar quantitative change of ammonium cyanate into carbamide.

On the other hand, from solutions of the fusion in warm water or alcohol the well defined compound $(CSN_2H_4)_3,NH_4SCN$ (m. p. 144°) was obtained. This forms characteristic, long needle-like crystals with satiny lustre, and was formerly regarded as impure thiocarbamide, being almost completely dissociated by further solution in water.

More recently Findlay (Trans., 1904, **84**, 403), from a careful study of the freezing points of a number of different mixtures of the two isomerides, arrived at the conclusion that the freezing-point curve of the two compounds is of the simplest form, melting at a eutectic point which he found to be 104·5°,* a result indicating the non-existence of any definite compound between the two isomerides in the liquid phase.

A mixture containing 52 per cent. of thiocarbamide was the richest in this isomeride, for which a freezing point (132°) was determined by Findlay, the course of the curve being completed by its extension in simplest form to meet the probable melting point of thiocarbamide, which he showed is not lower than 178°, and as a natural conclusion from the simple form of the freezing-point curve of the two isomerides as disclosed from the range of his experimental results, he states that from all mixtures of the two substances in the liquid phase containing more than 32 per cent. of thiocarbamide, this isomeride separates from the solution in fine, crystalline needles, quite different in appearance from the crystalline scales of ammonium thiocyanate which separate when the latter is in large excess.

Bearing in mind the readiness with which the well defined compound $(CSN_2H_4)_3,NH_4SCN$ can be extracted from the fused mass by water or alcohol, it seemed not unlikely that this compound is present in the mixture of the two isomerides in the liquid phase; if so, its existence would cause the freezing-point curve to deviate from the simple form obtained by Findlay, and as this investigator did not obtain points on his curve in the region of 75 per cent. of thiocarbamide, the existence of the above compound might have escaped his notice.

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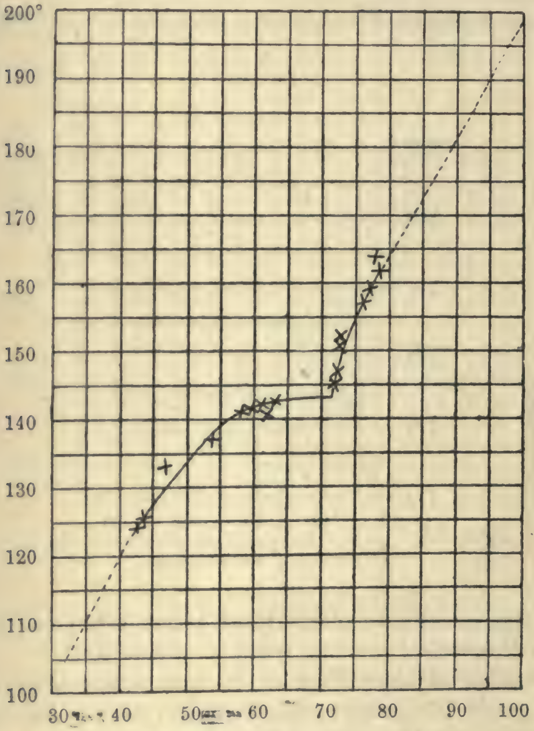
* Findlay found that a mixture having this freezing point contains 32 per cent. of thiocarbamide.

Accordingly, in order to obtain further evidence on this point, we have made a number of careful freezing-point determinations of mixtures of the two isomerides containing from 50 to 80 per cent. of thiocarbamide, the details of which are given in the experimental part of the paper.

The two curves (Figs. 1 and 2) plotted from the data obtained show a very marked deviation from the simple form of the freezing-point curve indicated by Findlay's experiments.

FIG. 1.



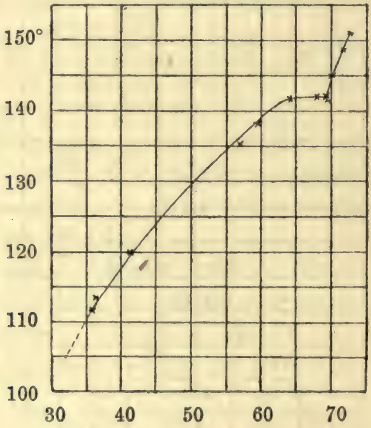
Percentage of thiocarbamide.

Our results show two curves intersecting at a point corresponding with about 70 per cent. of thiocarbamide, indicating the existence of the compound $(CSN_2H_4)_3,NH_4SCN$ in a partly dissociated condition in the fused material.

We have also satisfied ourselves that when the proportion of thiocarbamide in the liquid phase does not exceed 60 per cent. the thin, needle-like crystals which separate as the liquid cools are those of the above compound, and not crystals of thiocarbamide as Findlay supposed; as indicated by the curve, it is only when thiocarbamide exceeds the above proportion in the fusion that it separates in crystalline form as the liquid cools; a microscopic examination of the crystals in polarised light confirms this conclusion.

In addition to the form of the curve indicating the presence of the compound $(CSN_2H_4)_3,NH_4SCN$, it also shows clearly that the true melting point of thiocarbamide is experimentally unrealisable, a point to which Findlay (*loc. cit.*) has already referred, and from his experiments he places it at about 178°; our own results indicate a theoretical melting point at about 200°.

FIG. 2.



Percentage of thiocarbamide.

The reversion of thiocarbamide to ammonium thiocyanate commences at about 135°, and proceeds very rapidly as the temperature reaches 160°; for this reason it is also impossible to obtain the true melting point of mixtures of the two isomerides when fusion takes place at any temperature above 130°, at which point the reversion of thiocarbamide is practically nil within a reasonable limit of time. It is perhaps well to point out that this inversion of thiocarbamide only affects the accuracy of the determination of freezing points of mixtures of the two isomerides at comparatively very high temperatures, namely, about the region of 160°.

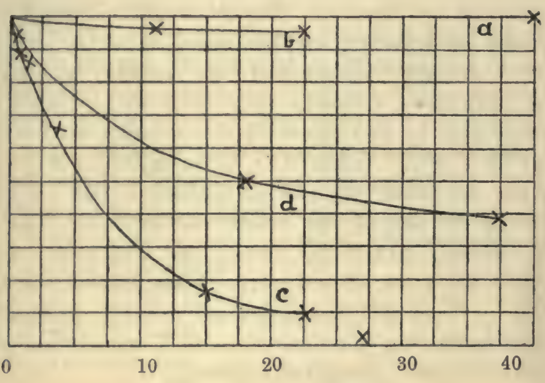
Although the compound $(CSN_2H_4)_3,NH_4SCN$ we find always melts sharply at 144°, the act of fusion is accompanied by a reversion of 12 per cent. of thiocarbamide; a change in composition therefore takes place before the true melting point can be reached.

Reversion of Thiocarbamide in Solution.

Some years ago we determined the extent of the reversion of thiocarbamide in aqueous and alcoholic solutions. The change was found to be almost complete in a normal aqueous solution at 142°; only 2·1 per cent. of thiocarbamide remained unchanged after twenty-seven hours, the reaction being unimolecular.

At 102°, the boiling point of a normal aqueous solution of thiocarbamide, the amount of reversion was very small even at the end of twenty-three hours, whilst at 60° no reversion could be even qualitatively detected at the end of three weeks; this behaviour is in marked contrast with that of carbamide.

FIG. 3.



(a) *Decomposition of normal aqueous solutions of thiocarbamide at* 60
(b) ,, ,, ,, ,, ,, 102
(c) ,, ,, ,, ,, ,, 140
(d) ,, *one-half and one-fourth normal alcoholic solutions of thiocarbamide at* 140°

These results were not published at the time, being to a certain extent just forestalled by the work of Dutoit and Gagnaux (*J. Chim. phys.*, 1906, **4**, 261); as these investigators did not examine the change in alcoholic solution, we give, for the sake of comparison, in Fig. 3, a graphical representation of the above results, together with the curve for the reversion in alcoholic solution.

The rate of reversion in a $N/2$- and $N/4$-solution was examined; the change was found to be much less rapid, 38·6 per cent. of thiocarbamide remaining unchanged after thirty-eight hours at

142°. The values for the two alcoholic solutions are plotted on the same curve, since, as the reaction is unimolecular, the velocity is independent of the absolute concentration.

At a higher temperature, or with more prolonged heating, secondary changes take place, resulting in the formation of thioalcohol, which interfere with the further examination of the reversion change.

Velocity of the Isomeric Change, $NH_4SCN \longrightarrow CSN_2H_4$.

The velocity constant of the above change was originally calculated by Waddell (*J. Physical Chem.*, 1898, **2**, 525) from experimental results, which on account of the imperfect method used for the estimation of thiocarbamide are less accurate than those subsequently obtained by Emerson Reynolds and Werner (*loc. cit.*), confirmed later by Findlay, and by ourselves in the present work.

We have therefore recalculated the velocity-constant of the change from the more accurate data, both by the simple unimolecular formula and by the equation for a balanced reaction given by Waddell (*loc. cit.*). Whilst the latter equation more accurately represents the course of the reaction, there is but little to choose between the constancy of the values afforded by both equations which are formally much the same. As the position of equilibrium is at 75 per cent. of ammonium thiocyanate, the only difference is that $\xi = 75$ is inserted instead of $a = 100$ (actually $a = 94{\cdot}8$ in the example taken).

The values obtained are given below:

$NH_4SCN \rightarrow CSN_2H_4$. $t = 170°$. $\xi = 75$ per cent. of NH_4SCN.

Time in minutes.	Percentage of NH_4SCN.	$K = \frac{1}{t}\log\frac{a.}{x - a}$	$K_1 = \frac{\xi}{at}\log\frac{\xi}{\xi - x}$.
0	94·8	—	—
5	92·1	0·0025	0·0024
10	87·2	0·0036	0·0034
15	84·1	0·0034	0·0033
20	81·8	0·0032	0·0031
25	80·2	0·0029	0·0028
30	78·3	0·0028	0·0027
		Mean value = 0·00307	Mean value = 0·00295

The value for K_1 given by Waddell varies from 0·00735 to 0·00564, with a mean of 0·00633; these much higher values may be in part attributed to the value $\xi = 78{\cdot}8$ found by him, instead of the more accurate number 75, found by Emerson Reynolds and Werner, whose experiments were carried out with a kilogram of material, with thermometers actually in the fusion; Waddell, on the other hand, used only 1 gram of material for each experiment. Whilst our numbers are much more uniform, the lower value of our constant is all the more remarkable, since the temperature of the fusion was 170°, as against 152°, the temperature at which Waddell's experiments were carried out.

Determination of the Association Factor.

In view of the fact that the compound $(CSN_2H_4)_3,NH_4SCN$ has been shown to exist in the fused mixture of the two isomerides, it seemed of interest to determine the association factor.

The method of Ramsay and Shields was not found practicable in this case, on account of the unavoidable accumulation of minute bubbles of gas in the capillary tube at temperatures somewhat above the eutectic point.

Using Traube's atomic volumes,* however, and employing the value D_{15}^{105} 1·231 for the density of the fusion at the eutectic point, it was found that the molecular weight of the complex is 298; an association factor $n=4$ would give 304. Accordingly, the ammonium thiocyanate molecules are presumably associated like with like,† as well as forming a definite compound. It is perhaps well to point out that the eutectic mixture contains a large excess of ammonium thiocyanate, the presence of which diminishes the dissociation of the compound.

Compounds of Thiocarbamide with Rubidium and Caesium Iodides.

The influence of certain salts on the reversion of thiocarbamide and ammonium thiocyanate respectively is at present under investigation, but although the results are not yet sufficiently complete for publication, we take this opportunity of placing on record the existence of two new compounds which we have incidentally prepared in connexion with this work, and which complete the series of tetra-thiocarbamide compounds, the original member of which, $(CSN_2H_4)_4,NH_4Br$, was first obtained by Emerson Reynolds (Trans., 1891, **59**, 385).

The compound $(CSN_2H_4)_4,KI$ (m. p. 189°) has already been described by one of us (Werner, Proc., 1906, **22**, 245); we have now to add the analogous compounds:

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* This method has already been tested for several pairs of organic substances by one of us (Atkins, Proc., 1910, **26**, 338), and was found to give results in agreement with that afforded by freezing-point determinations.

† Since the compound contains only 25 per cent. of NH_4SCN, whilst the eutectic mixture contains 75 per cent., it is clear that the molecules of excess of thiocyanate, namely, 75 per cent. less 8·3 per cent. required to combine with the thiocarbamide, must be associated, for the whole fusion gives an association factor $n=4$.

$(CSN_2H_4)_4,CsI$ (m. p. 191°) and $(CSN_2H_4)_4,RbI$ (m. p. 202°), which crystallise from alcoholic or concentrated aqueous solutions in long, delicate needles with the characteristic satiny lustre peculiar to all these tetrathiocarbamide additive compounds.

Sodium iodide, as has already been pointed out (Werner, *loc. cit.*), does not form any compound with thiocarbamide, and in this respect we find that lithium iodide resembles the sodium salt. This peculiar difference of sodium and lithium as compared with the three other alkali metals is certainly not without interest, bearing in mind the general relations of the members of this group of metals. We have also obtained the compound $(CSN_2H_4)_3,KSCN$ (m. p. 143°), which crystallises from alcoholic solution in delicate needles resembling its ammonium analogue.

EXPERIMENTAL.

In determining the freezing point of mixtures of thiocarbamide and ammonium thiocyanate, Findlay found that it was sufficient to heat to fusion previously prepared mixtures of the two isomerides of known composition, and note the temperature at which crystals appeared; this method gives accurate results provided the freezing point does not exceed 135°, which is the limit of his experiments.

For reasons already stated, this method could not be adopted for the purpose of obtaining the information we required.

The mode of procedure was as follows: A quantity, about 20 grams, of pure thiocarbamide was quickly heated to fusion in a wide test-tube immersed in a bath of phenol; at intervals the tube was raised just above the level of the hot liquid, and allowed to cool while being kept well stirred by means of the thermometer; as soon as the freezing point was reached a portion of the fusion was withdrawn by means of a cold glass rod dipped into the liquid; in this way sufficient material for analysis could be removed with the minimum loss of time, which was an absolutely necessary precaution on account of the rapid change in composition at the higher temperatures.

Thirty freezing-point determinations were thus obtained, ranging from 164° to 111·6°; in many cases the experiments were repeated in order to check the accuracy of the results.

The thiocarbamide was estimated by means of standard solution of iodine, according to the method originally devised by Emerson Reynolds and Werner (*loc. cit.*). Two series of freezing-point determinations were made. In Series I, from which curve I is plotted, the freezing point was taken as that temperature at which small crystals appeared throughout the whole of the well-stirred, clear fusion, supercooling being avoided by the presence of crystals on the sides of the tube at the level of the meniscus. The tube was surrounded by the hot phenol vapour while cooling. In Series II, from which curve II is plotted, the freezing point was taken to be the steady temperature that was reached, and maintained for a while, as the liquid began to solidify; this temperature was always slightly lower than that obtained in Series I for obvious reasons, and the divergence was greatest at the high temperatures where the effect of the cooling was most rapid.

The results of our freezing-point determinations are given in the following tables:

Series I.

Thiocarbamide. Per cent.	Freezing point.	Thiocarbamide. Per cent.	Freezing point.
77·8	164·0°	63·0	142·5°
*78·2	161·5	61·0	142·0
77·1	159·0	59·3	141·5
76·9	158·0	58·1	141·3
76·4	157·0	*61·8	140·5
*72·6	152·0	54·0	137·0
73·1	150·0	46·7	133·0
72·4	147·0	43·5	125·5
71·9	145·0	42·6	124·5

* These results are no doubt due to experimental error, see page 1177.

Series II.

Thiocarbamide. Per cent.	Freezing point.	Thiocarbamide. Per cent.	Freezing point.
72·8	151·0°	64·0	141·0°
71·8	148·5	59·5	138·0
70·0	145·0	57·0	135·2
69·2	142·0	41·3	119·8
68·5	141·8	36·3	113·3
68·1	141·7	35·8	111·6

The values obtained in both series of experiments, represented graphically in Figs. 1 and 2, are practically identical, in so much that they show conclusively a departure from the simple form of the curve slightly beyond the limit (52 per cent. of thiocarbamide) of Findlay's experiments, and indicate the presence of a compound near the region of 75 per cent. of thiocarbamide. No doubt the compound $(CSN_2H_4)_3,NH_4SCN$ is present in the liquid phase below 145°, and partly dissociated a few degrees below its melting point, as shown by the flatness of the curve in this region. Between 130° and 104·5°, the eutectic point, our results are in perfect agreement with those of Findlay as regards the direction of the curve, which, however, is not that of a mixture of the two isomerides, but of the compound $(CSN_2H_4)_3,NH_4SCN$, which is moderately stable between these temperatures, dissociation diminishing with fall of temperature and presence of excess of ammonium thiocyanate. In order further to test this point, the two following experiments were made, the results of which, in addition to being foreshadowed by the nature of the curve, prove its accuracy and confirm our conclusion regarding the existence of the above compound.

Analysis of the Crystals which separate from the Liquid Phase containing (a) *below,* (b) *above* 70 *per cent. of Thiocarbamide.*

Experiment (*a*).—Twenty-five grams of an intimate mixture containing 60 per cent. of thiocarbamide and 40 per cent. of ammonium thiocyanate were quickly heated in a short wide test-tube to complete liquefaction (140°); the temperature was raised for a few moments to 144°, after which the liquid was allowed to cool; at 136° (the freezing point) needle-like crystals commenced to separate, when the liquid was quickly poured off into another vessel, leaving a certain amount of solid matter in the tube, from which it was possible to detach a small quantity of well defined acicular crystals. These and the liquid poured off from them were analysed:

	In acicular crystals.	In liquid poured off.
Percentage of thiocarbamide	59·9	50·2

Whilst it is quite out of the question to expect anything approaching purity in the separated crystals, on account of the rapid solidification which takes place as soon as the tube is removed from the source of heat, it is evident that the crystals which separated from the fused material could not be thiocarbamide, contaminated to such an extent as indicated by the analysis with material containing more than 50 per cent. of the substance. That they are impure crystals of the compound $(CSN_2H_4)_3,NH_4SCN$ is beyond doubt.

Experiment (*b*).—Ten grams of pure thiocarbamide, in fine powder, were quickly introduced into a wide test-tube immersed in a bath of glycerol previously heated to 170°; complete fusion of the thiocarbamide was thereby effected within eight minutes, after which the liquid was allowed to cool. At 159° crystals commenced to appear, and were dealt with as in the previous experiment; it was not possible to separate any needle-like forms, but some small crystals were detached from the solid round the wall of the tube. These and the liquid poured off from them were analysed:

	In detached crystals.	In liquid poured off.
Percentage of thiocarbamide	81·8	69·1

Whilst the difficulty of separating the crystals is even greater in this case than in the former experiment, it is evident that they are crystals of thiocarbamide contaminated with adherent material containing slightly more than 69 per cent. of that substance.

The fused material from both experiments was separately dissolved in slightly more than its own weight of hot water, and the solutions allowed to cool.

From (*a*) long, delicate, needle-like crystals with satiny lustre were deposited (m. p. 144°); these contained 74·96 per cent. of thiocarbamide, and were therefore the pure compound

$$(CSN_2H_4)_3,NH_4SCN;$$

from (*b*) practically pure thiocarbamide separated in the familiar form of short, stout, rhombic prisms quite free from any needle-like forms.

Thus, whilst Findlay was led to the conclusion that thiocarbamide is the substance that separates from fused mixtures of the two isomerides until its concentration falls below 32 per cent., our results show that this is only true when the concentration is not less than about 65 per cent.; below this and down to the eutectic point (104·5°) it is the compound $(CSN_2H_4)_3,NH_4SCN$ that separates in crystalline form.

For reasons already stated, a high degree of accuracy is not to be expected in the determinations of freezing points at the higher temperatures; the withdrawal of a portion of the fusion for analysis and the temperature reading were performed as simultaneously as possible; nevertheless, a few irregularities appear, which, however, do not affect the general accuracy of the curve. We may point out that these only occur among the determinations of Series I, where the difficulty is greatest in taking an accurate temperature reading simultaneous with the removal of material, the former falling rapidly as crystallisation proceeds.

Preparation and Properties of Tetra-thiocarbamide Compounds of Rubidium and Caesium Iodides.

The following compounds are readily prepared by mixing hot alcoholic solutions of the respective iodides with a warm alcoholic solution of thiocarbamide. The new additive compounds separate as the solutions cool in delicate needles with beautiful, satiny lustre. They were purified by recrystallisation.

The *rubidium* compound, $(CSN_2H_4)_4,RbI$, melts at 202°:

0·5075 gave, on distillation with ferric sulphate, 0·1245 I. I = 24·52.

$C_4H_{16}N_8S_4,RbI$ requires I = 24·62 per cent.

The *caesium* compound, $(CSN_2H_4)_4,CsI$, melts at 191°:

0·3923 gave 0·0876 I. I = 22·33.

$C_4H_{16}N_8S_4,CsI$ requires I = 22·48 per cent.

In both cases fusion is accompanied by very rapid decomposition, that is, reversion of the thiocarbamide; these melting points were obtained by immersing the melting-point tubes in a bath of glycerol heated almost to the temperature to be determined.

Although both compounds are completely dissociated in dilute aqueous solution, they may be crystallised unchanged from concentrated solutions, a remark which also applies to the compound $(CSN_2H_4)_4,KI$ (m. p. 189°).

Whilst the thiocarbamide rapidly undergoes reversion at the respective melting points of these compounds, as might be expected, nevertheless it is more stable in these compounds than in the free state; for example, prolonged heating of the compound

$$(CSN_2H_4)_4,KI$$

at 142° failed to produce any reversion of the thiocarbamide to ammonium thiocyanate, whilst thiocarbamide itself when kept for half an hour at this temperature undergoes reversion to the extent of 4 to 5 per cent.

These changes, together with the effect of other saline compounds on the reversion of thiocarbamide and ammonium thiocyanate, are at present under investigation.

Preparation of a Compound of Thiocarbamide and Potassium Thiocyanate.

Thiocarbamide and potassium thiocyanate are dissolved in alcohol, and the solution heated to boiling under a reflux condenser for about half an hour. The additive compound separates as the solution cools in thin needles with satiny lustre. When purified by recrystallisation it melts at 143°:

0·25 gave, on titration with standard iodine solution, 0·1748 CSN_2H_4. CSN_2H_4 = 69·92.

0·2 gave 0·103 AgSCN. SCN = 17·99.

$(CSN_2H_4)_3KSCN$ requires CSN_2H_4 = 70·15; SCN = 17·84 per cent.

This tri-thiocarbamide compound is therefore analogous to that which thiocarbamide forms with ammonium thiocyanate.

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CXXIV.—*Properties of Mixtures of Allyl Alcohol and Water. Part I.*

By Thomas Arthur Wallace and William Ringrose Gelston Atkins.

With the exception of some rough work by Rylands (*Amer. Chem. J.*, 1899, **22**, 384) on binary mixtures of allyl alcohol with benzene and toluene, and a passing reference by Konowaloff (*Ann. Phys. Chem.*, 1881, [iii], **14**, 34) and others to the existence of a binary with water, we have been unable to find any work dealing with this subject. However, as the alcohol is only prepared in the pure state by a tedious distillation, and as there are many points of interest in the behaviour of such mixtures, we decided to study the matter further.

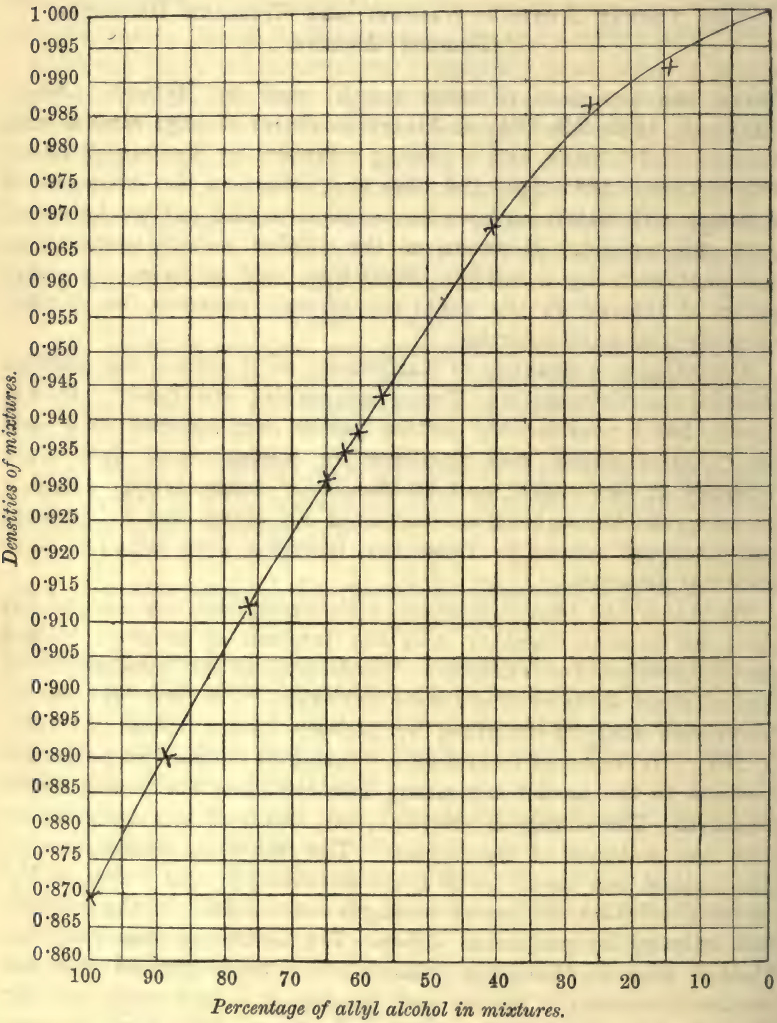
Accordingly, a quantity of Kahlbaum's allyl alcohol was distilled through an eight-section Young evaporator still-head. It was found that a considerable portion passed over between 96·3° and 96·7°, after which two distillates of almost equal bulk were collected at 96·7—96·8° and 96·80—96·87° respectively. (Boiling points given throughout are corrected for errors due to pressure and emergent column.) These two fractions were found to have identical densities.

To obtain the binary mixture with water, the two components must be distilled together, and the fraction of constant boiling point preserved for analysis. To determine the constitution of this mixture three methods were available. The first was one by volumetric analysis described by Mabery (*Amer. Chem. J.*, 1883, **5**, 262). It consisted in adding a solution of bromine in potassium bromide to the alcohol-containing mixture until the brown colour persisted. The change is complete, two atoms of bromine reacting with one molecule of the alcohol. The following modification of this method was found to be quite satisfactory. An excess of the bromine solution of known strength was added to the alcohol, and followed by potassium iodide. The iodine set free was then titrated with $N/10$-sodium thiosulphate. Trials showed that the reaction between the alcohol and bromine is a very rapid one, for addition of the iodide immediately and after an hour gave identical results. Details of suitable quantities are given in the experimental portion.

The second method was to construct a curve showing the densities of weighed mixtures of allyl alcohol and water, then to determine the densities of the various distillates, and read off their compositions from this curve.

These two methods are, of course, perfectly general for obtaining the composition of any mixture; the third is applicable of necessity to the binary mixture only, and is the middle-point distillation method of S. Young ("Fractional Distillation," Chapter XVI.). As the subsequent work depends on the density-composition diagram, it will be considered first.

FIG 1.

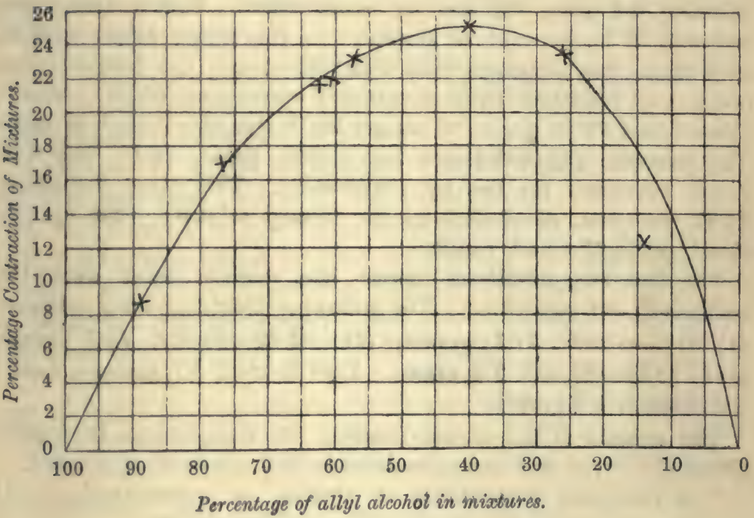


The Densities of Mixtures of Allyl Alcohol and Water.

The following graphs are constructed to show the densities and contractions of the alcohol–water mixtures as mentioned before. The data will be found in the experimental portion.

It will be noticed that the contraction curve is almost straight, and quite steep up to a mixture containing 76·69 per cent. of alcohol. This percentage corresponds with an equimolecular mixture of the two substances. The slope then becomes less steep, continuing to rise to a maximum at 39 per cent. of alcohol, where the contraction amounts to 2·54 per cent., calculated on the theoretical volume of the mixture. From this onwards there is a regular fall, quite unlike the rising portion.

FIG. 2.



The Distillation of Allyl Alcohol and Water.

Preliminary experiments having shown that the binary mixture distilled at about 88·8° and contained roughly over 68 per cent. of alcohol, a mixture of the alcohol and water of known composition, water being in excess, was distilled through an eight-section evaporator still-head. The following fractions were collected:

1st.	Up to 94·4 (the middle point taken)	107·29 grams
2nd.	Above 94·4, residue in still	18·23 ,,
	Total.........	125·52 grams

Original mixture: Water, 50·1 grams; alcohol, 77·8 grams (namely, 60·83 per cent.); total, 127·9 grams; loss, 2·4 grams. This somewhat large loss may perhaps be accounted for by the fact that too large a flask was used in the distillation. The weight below the middle point was accordingly 107·8 grams, allowing 0·5 gram for loss by evaporation (see Young, "Fractional Distillation"). Calculation from these data gives as the composition of the binary mixture, $\frac{77\cdot8 \times 100}{107\cdot8} = 72\cdot2$ per cent. of alcohol.

Allyl alcohol and water were then mixed, 64·90 grams of the former to 11·68 grams of the latter, alcohol thus being in excess, and were distilled through a five-section column up to the middle point, namely, 92·6°. In this manner 49·38 grams were obtained, allowing 0·3 gram for loss by evaporation. Hence the binary contains 76·35 per cent. of alcohol. As this figure differs considerably from that obtained with water in excess, the former experiment was repeated with a mixture containing 30·56 grams of alcohol and 42·20 grams of water, the latter thus being in excess. The amount collected below the middle point, 94·4°, was 42·52 grams corrected for loss by evaporation. This gives accordingly 71·87 per cent. of alcohol in the binary mixture, thus agreeing closely with the first result.

The last two distillates below the middle point were then combined and redistilled. The following fractions were collected: (I) 87·9—87·99°, 11·1 grams; (II) 87·99—88·01°, 66·7 grams; (III) 88·01—88·03°, 6·3 grams. Left in still, 5·7 grams. Loss in distillation, 1·6 grams.

The density of the second fraction was found to be D_0^0 0·91887. From the curve this corresponds with 72·0 per cent. of alcohol.

The foregoing percentages of alcohol, as ascertained by the middle-point method, may be summarised as follows:

	Allyl alcohol. Per cent.
1. Water in excess	72·2
3. ,, ,, ,,	71·9
2. Alcohol in ,,	76·3
Mean, omitting No. 2	72·05

The discrepancy in the distillation with alcohol in excess is probably due to the small difference between the middle point taken, 92·6°, and the boiling point of the alcohol, 96·4°, as commonly taken. The subsequent more exact determinations of the boiling point of the binary, 88·0°, instead of 88·8°, and of the alcohol, 96·95°, instead of 96·4°, give as middle point 92·5°. Accordingly it seems better to reject the result of this distillation.

On the other hand, although the true middle point with water in excess was 94·0°, instead of 94·4°, yet as the temperature rise in this case was extremely rapid the error thus introduced is negligible. As from the density the percentage of alcohol is 72·0, whilst the mean of the middle-point method determinations gives it as 72·05, we may conclude that the binary mixture contains 72·0 per cent. of allyl alcohol.

Conclusion.

Pure allyl alcohol has D_0 0·86929, and boils at 96·95°. It forms a mixture of constant boiling point with water, containing 72·0 per cent. of the alcohol, and boiling at 88·0°. Mixtures with water show a large contraction in volume, the maximum being 2·54 per cent. at a concentration of 39 per cent. of alcohol when determined at 0°.

EXPERIMENTAL.

The Volumetric Estimation of Allyl Alcohol.

The solutions used were as follows:

A. About 20 grams of bromine and 30 grams of potassium bromide per litre.

B. Fifty grams of potassium iodide per litre.

The exact strength of the bromine solution was found by adding 10 c.c. to excess of potassium iodide. The value obtained was 21·32 grams per litre. Below are given examples estimated as described in the earlier portion of the paper.

(1) Alcohol taken, 3·168 grams; found, 3·192 grams. An hour was allowed to elapse before adding the iodide solution.

(2) Alcohol taken, 3·067 grams; found, 3·087 grams. In this case the iodide was added immediately. The above analyses both give results which are slightly too high; accordingly, a fresh solution of thiosulphate was standardised against a weighed amount of Kahlbaum's iodine, and two further estimations made.

(3) Alcohol taken, 0·2350 gram; found, 0·2330 gram. Error, −0·0020 gram.

(4) Alcohol taken, 0·2886 gram; found, 0·2950 gram. Error, +0·0064 gram. Considering the small quantities used, these results may be considered to be satisfactory.

Determination of the Densities of Mixtures of Allyl Alcohol and Water.

Below are recorded the densities as found by means of a Sprengel tube with bulb to permit of expansion of the liquid above the mark as described by W. H. Perkin (Trans., 1884, **45**, 444). The figures are corrected to weight in a vacuum. D^0_0 was then corrected to D^0_4 from which the volume of a gram of each mixture may be obtained. D^0_4 (calc.) was found by the usual formula:

$$\frac{w_1 + w_2}{D} = \frac{w_1}{D_{(1)}} + \frac{w_2}{D_{(2)}},$$

neglecting contraction.

The calculated volume of a gram was obtained in this manner, and the difference between the observed and calculated volumes of a gram expressed as a percentage of the latter value is recorded as the contraction. The allyl alcohol was obtained from Kahlbaum, and was distilled as described; it boiled at 96·80—96·87°.

Table of Densities and Contractions.

I. Alcohol Per cent.	II. D^0_0. found.	III. D^0_4. found.	IV. D^0_4. calc.	V. Vol. of a gram found.	VI. Vol. of a gram calc.	VII. Contraction. Per cent.
0·00	1·00000	0·999868	0·999868	1·0001	1·0001	0·000
14·24	0·99134	0·99121	0·97893	1·0089	1·0215	1·233
26·16	0·98560	0·98547	0·96206	1·0147	1·0394	2·376
40·30	0·96758	0·96746	0·94280	1·0337	1·0606	2·536
57·00	0·94317	0·94305	0·92102	1·0604	1·0858	2·339
60·51	0·93755	0·93743	0·91657	1·0668	1·0910	2·218
62·49	0·93455	0·93443	0·91407	1·0702	1·0940	2·176
65·05	0·93089	0·93077	0·91088	1·0744	1·0976	2·132
76·69	0·91235	0·91223	0·89659	1·0962	1·1153	1·712
88·90	0·89008	0·88996	0·88210	1·1236	1·1337	0·891
100·00	0·86942	0·86931	0·86931	1·1503	1·1503	0·000

The Sprengel tubes employed held about 14 grams of water. Their volumes were checked during the course of the work. Three determinations of density on the same sample of pure alcohol gave the results recorded below:

$$\left.\begin{array}{l}\text{1st. } D^0_0\ 0{\cdot}86942 \\ \text{2nd. } D^0_0\ 0{\cdot}86943\end{array}\right\}\ \text{b. p. } 96{\cdot}80\text{—}96{\cdot}87^\circ \text{ corrected.}$$

3rd. D^0_0 0·86929 after redistillation with five-section still, b. p. 96·93—96·95°. The density as found above may be compared with the value D^0 0·87063 obtained by Thorpe (Trans., 1880, **37**, 210).

The behaviour of this alcohol on distillation with benzene and with benzene and water is being investigated, and we hope shortly to be able to give complete results.

In conclusion, we wish to express our thanks to Prof. Sydney Young for the use of apparatus, and for the benefit of his advice during the progress of the work, which was carried out in his private laboratory.

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CXXV.—*The Vapour Density of Ammonium Nitrite.*

By Prafulla Chandra Rây, Nilratan Dhar, and Tincowry De.

One of us has already shown that ammonium nitrite can be sublimed in a vacuum at a temperature of 37—40° (Rây, Trans., 1909, **95**, 345). This property suggested to us the possibility of the determination of its vapour density in Hofmann's apparatus under very reduced pressure. Neogi and Adhicary (Trans., 1911, **99**, 118) attempted to determine the vapour density of ammonium nitrite at different temperatures, but their experiments did not lead to any satisfactory results. It will be conducive to the proper understanding of what follows later if some of the properties of ammonium nitrite are first given in detail.

Ammonium nitrite obtained from the double decomposition of ammonium chloride and silver nitrite crystallises from its saturated solution when kept in a vacuum desiccator with a distinct yellowish-green tint. In connexion with this it is interesting to note that methylammonium nitrite almost exactly resembles ammonium nitrite in external appearance (compare Trans., 1911, **99**, 1018). The substance gradually changes into the nitrate. Even during the process of crystallisation, which generally requires two to three days, traces of ammonium nitrate are formed, and the higher the laboratory temperature the larger is the amount of the latter. It is very deliquescent. When heated in the ordinary way, it decomposes mainly into nitrogen and water, but there is also a side-reaction, as observed by Rayleigh and Ramsay in their classical experiments on the preparation of "chemical" nitrogen by heating an aqueous solution of potassium nitrite and ammonium chloride. These experimenters distinctly smelt ammonia among the products (*Phil. Trans.*, 1895, **186**, *A*, 189). The side-reaction evidently proceeds according to the equation:

$$3NH_4NO_2 = NH_4NO_3 + 2NO + 2NH_3 + H_2O.$$

The ordinary salt, when subjected to a gradual rise of temperature in a tube connected with a Sprengel air-pump, begins to sublime at about 32° to 33°. The temperature of the bath can be safely raised to 60° without the substance undergoing decomposi-Fine crystals are deposited, and grow to a transparent, compact mass on the cooler part of the tube, which is artificially kept cool to avoid a portion of the sublimate being carried away into the "fall-tube" in the shape of fine dust. There is left a small residue consisting of ammonium nitrate due to what was present in the original salt, as the "click" throughout the process of sublimation remained persistent.

The pure sublimed salt is quite colourless, and absolutely devoid of the green tint. It is less hygroscopic, and far less liable to decomposition than the ordinary salt. When kept open in a desiccator the sublimed substance does not change, even after the lapse of five or six days, but slowly diminishes in weight from day to day. When kept, however, in a vacuous sealed tube, the salt can be preserved for any length of time.* The crystals in the vacuum tube can be made to pass from one part to another by the application of gentle heat. The pure salt can be resublimed in a vacuum without any decomposition or residue of ammonium nitrate, provided the temperature of the bulb does not exceed 60°.

Ammonium nitrate under similar conditions does not vaporise or decompose. This difference in property has been utilised in completely separating ammonium nitrite from the nitrate, with which it is often more or less admixed.

EXPERIMENTAL.

In the determination of the vapour density, however, the condition is somewhat different from what obtains in the vacuum of the Sprengel pump. Here the continuity of the vacuum is not maintained, for the vapour itself, as well as its decomposition products, are not removed as soon as they are produced. Consequently, when ammonium nitrite is heated in the Hofmann tube, a part breaks up into nitrogen and water; a very small fraction at the same time decomposes into ammonium nitrate, ammonia, nitric oxide, and water, according to the equation given above, and the rest vaporises.

In a series of preliminary experiments, small quantities of ammonium nitrite were introduced into the Hofmann tube and heated to 100° until the volume remained constant. When cooled, a solution of potassium iodide acidified with dilute sulphuric acid was introduced; and in these experiments iodine was seen to be liberated each time. Evidently, therefore, some part at least of the nitrite remained undecomposed.

Baker (Trans., 1894, **65**, 612; 1900, **77**, 646; 1902, **81**, 400), in a series of memorable researches, has shown that moisture plays an important part in many chemical reactions, and that the abnormal vapour density of ammonium chloride and of mercurous chloride becomes normal when these are perfectly dry. From the present experiments, however, it will be seen that so far as ammonium nitrite is concerned, the presence of moisture does not seem to affect the vaporisation. Moreover, Neuberg (*Ber.*, 1891, **24**, 2543) has determined the vapour density of ammonium chloride, which is not perfectly dry (in the Bakerian sense) under reduced pressure in an apparatus devised by himself and Lunge. His results show conclusively that the molecule of ammonium chloride can exist in the gaseous state (compare also *Annual Reports*, 1911, 28).

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* The walls of the tube on close inspection are, however, found bedewed with moisture due to a slight decomposition of the substance.

From blank experiments it was seen that ammonium nitrate has appreciable vapour pressure at 100°. The steam was therefore replaced by alcohol vapour; at this temperature the vapour pressure of ammonium nitrate is practically nil.

In these experiments at 78° we get a mixture of ammonium nitrite vapour, nitrogen, water vapour, nitric oxide, and ammonia, besides a little air always admitted along with the substance in the Hofmann bottle. One-fifth of this air, which is oxygen, is taken up by the nitric oxide to form nitrogen peroxide; the latter in its turn gives up the oxygen to the mercury, which is thus often found to be very slightly tarnished on the surface. At this temperature and low pressure the whole of the water is in the state of unsaturated vapour.

When, however, the tube was cooled to the ordinary temperature (31°), particles of moisture were seen to be deposited on the inner walls of the tubes, so that the space was now saturated. Blank experiments also proved that ammonia is practically not absorbed by this moisture at this temperature and under such a diminished pressure. The undecomposed ammonium nitrite now condenses, and dissolves in the water.

The nitric oxide was absorbed by about 0·5 c.c. of alkaline sodium sulphite solution.* The tube was then inverted over a cylinder containing water. The residual gas was pure nitrogen.

The vapour density of ammonium nitrite was also taken at 66° by surrounding the Hofmann tube with methyl alcohol vapour.

It was also noticed that if after heating the tube for a short time it was suddenly cooled, crystals of ammonium nitrite were deposited on the inner walls.

The time for attaining constant volume in the case of the ordinary salt was four to five hours, and in the case of the compact sublimed salt an hour or so more.

Altogether, some twenty experiments were made. We give below the full data of a typical experiment, from which the result has been calculated.

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* Several blank experiments were made in which about 1 to 0·5 c.c. of pure nitric oxide was introduced into the Torrecellian vacuum. On introducing 0·5 c.c. of sodium sulphite solution and gently shaking, the nitric oxide was completely absorbed.

Weight of substance taken = 0·014 gram. Analysis showed that it contained 0·013 gram of real nitrite:

(*a*) Volume of air = 0·45 c.c. at N.T.P.

(*b*) Volume of gas surrounded by ethyl alcohol vapour at 78° = 12·104 c.c. at N.T.P.

(*c*) Volume of gas when cold at 31° = 4·439 c.c. at N.T.P.

(*d*) Volume of gas after absorption of nitric oxide by alkaline sulphite solution and of ammonia by water = 3·82 c.c. at N.T.P.

Now in (*a*) during the experiment the air was deprived of its oxygen as noted above, and became four-fifths of the original volume, that is, we get only 0·36 c.c.

The volume in (*b*) consisted of nitrogen and unsaturated water vapour (due to the decomposition of the salt), ammonia, nitric oxide, and unsaturated water vapour (due to the side-reaction decomposition), air minus its oxygen, and undecomposed ammonium nitrite vapour.

The volume in (*c*) consisted of nitric oxide, ammonia, nitrogen due to decomposition, and air minus its oxygen, all in the moist state.

The volume in (*d*) consisted of nitrogen due to decomposition, and also that of the air, in the moist state.

From (*a*) and (*d*) we get nitrogen due to decomposition alone,

3·82 c.c. − 0·36 c.c. = 3·46 c.c.

The amount of ammonium nitrite decomposed to produce this volume of nitrogen is 0·0099 gram according to the equation

$$NH_4NO_2 = N_2 + 2H_2O.$$

From (*c*) and (*d*) we get ammonia and nitric oxide = 4·439 c.c. − 3·826 c.c. = 0·613 c.c. Therefore, the volume of nitric oxide or ammonia alone = 0·306 c.c.

The amount of ammonium nitrite decomposed to produce this volume of nitric oxide or ammonia = 0·0013 gram, according to the equation:

$$3NH_4NO_2 = NH_4NO_3 + 2NO + 2NH_3 + H_2O.$$

Thus we see that of 0·013 gram of ammonium nitrite, 0·0099 and 0·0013 gram respectively were decomposed, and only 0·013 − 0·0099 − 0·0013 = 0·0018 gram was left undecomposed.

The volume actually occupied by this weight of ammonium nitrite in the vaporised state has now to be determined.

Volume of (*b*) 12·104 c.c. = 3·46 c.c. of nitrogen due to decomposition, + 0·36 c.c. of nitrogen from air in the Hofmann bottle + (6·93 + 0·153) c.c. of water vapour + 0·306 c.c. of ammonia + 0·306 c.c. of nitric oxide + the volume occupied by the ammonium nitrite vapour. Therefore volume of ammonium nitrite vapour = 0·589 c.c.; but 22400 c.c. at N.T.P. is the volume of 1 gram-molecule. Therefore the molecular weight of ammonium nitrite

$$= \frac{22400 \times 0{\cdot}0018}{0{\cdot}589} = 68{\cdot}45$$

and Density = 34·22.

The result of a few more experiments are tabulated below:

No.	Substance, milligram.	Amount undecomposed, milligram.	Volume of undecomposed salt at N.T.P., c.c.	Density.
I.	13·0	3·26	1·14	32·0
II.	12·6	2·30	0·813	34·0
III.	13·4	1·14	0·393	32·7
IV.	14·0	1·80	0·607	33·0
V.	9·7	1·80	0·573	35·0

The mean value therefore of the vapour density is 33·5, whereas the theoretical value is 32·0.

It will thus be seen that ammonium nitrite vaporises without dissociation.

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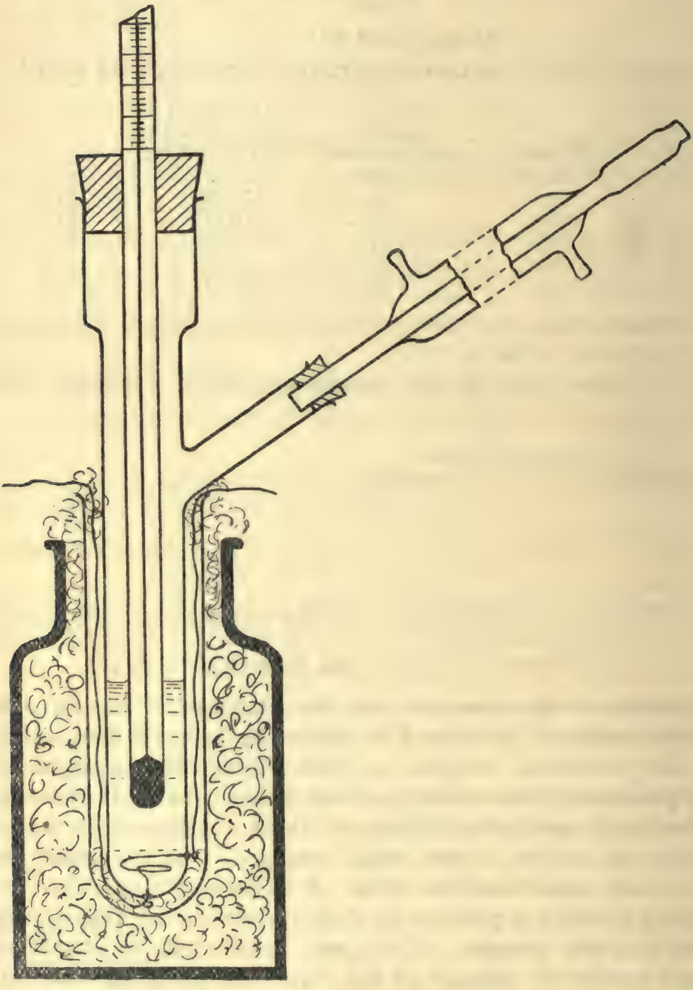
CXXVI.—*A Modification of the Beckmann Apparatus.*

By Edmund Knecht and John Percy Batey.

In the course of a research into the condition of certain dyes in aqueous solution, we desired to make ebullioscopic determinations of their molecular weights by determining the elevation which they produced in the boiling point of water. Owing to the complex nature and sparing solubility of these substances, it was only possible to produce a very small rise in the boiling point, and it was found that with the types of Beckmann apparatus at our disposal it was not possible to obtain a sufficiently regular boiling point for this purpose. This was attributed to superheating effects caused by cohesion of the liquid on the glass walls of the containing vessel. To avoid this we were led to try an electric heating method, in which the heat is supplied by a platinum wire in direct contact with the solution.

A tube was made with a platinum heating coil inside, whilst somewhat thicker wires fused through the glass were employed in making the necessary connexions.

When in use the apparatus rested in an outer cylindrical glass jacket, which itself rested in a wide-mouthed bottle, packed at the bottom and round the neck with cotton-wool (see diagram). It was found that with this arrangement the boiling point of the solution remained constant to 0·001°.



We subsequently found that electric heating had been used before for this purpose. S. L. Bigelow (*Amer. Chem. J.*, 1899, **22**, 208) first used the method and demonstrated its usefulness. Later the subject was more fully discussed by E. Beckmann (*Zeitsch. physikal. Chem.*, 1908, **63**, 177). Both these experimentors state that the method is not applicable for use with aqueous solutions.

Thus, Bigelow says: "Electric heating is not applicable for use with water solutions, for difficulties due to electrolysis would be sure to be encountered."

Beckmann found that a solution of potassium bromide was instantly turned brown when a current of 2 amperes was passed through the heating coil; and this took place even when alternating current was used. We repeated the experiment with potassium bromide in our apparatus with a direct current of 7 amperes, and not a trace of bromine was liberated. In view of this fact we were led to compare the physical constants of Bigelow's and Beckmann's apparatus with those of our own.

Bigelow and Beckmann both used a heating coil of 5 ohms resistance. The current used by Beckmann to produce the necessary heating effect was:

1½ amperes for low boiling solvents.
2 „ „ high „ „

In our apparatus the resistance of the heating coil at 100° was 0·47 ohm. The current used was 6·5 amperes. Hence the drop in potential across the coil was only 3 volts.

Evidently the electrolytic effect will depend on the drop in potential across the heating coil, and when this is reduced below a certain point (for potassium chloride about 2½ volts) theoretically no electrolysis should take place.

The following experiments were done with a view to ascertaining how much electrolysis actually took place in our apparatus.

A 10 per cent. solution of potassium chloride was introduced into the boiling tube and a current of 7 amperes passed for forty-five minutes. The liquid was then titrated for chlorate by means of titanous chloride, and it was found that only 0·2 per cent. of the potassium chloride had been converted into chlorate.

A 10 per cent. solution of potassium iodide was treated with 7 amperes for thirty minutes. The liquid was then titrated for iodine (after acidifying) by means of thiosulphate. The amount of iodine found (free and as iodate) was only 0·5 per cent. of the weight of potassium iodide taken.

A 2 per cent. solution of crystal-scarlet was treated for thirty minutes with 6½ amperes, and was then titrated with titanous chloride; 1·5 per cent. of the dye had been destroyed. Benzopurpurine gave similar results. In the above experiments the currents used are slightly greater and the time much longer than would be the case in carrying out a determination. It is evident, therefore, that by using a heating coil of low resistance the amount of electrolysis which takes place during a determination is negligible.

In another apparatus the resistance of the heating coil was still less, being only 0·32 ohm. With a current of 7½ amperes this would correspond with a drop in potential across the coil of 2·2 volts. With a 10 per cent. solution of potassium chloride and boiling for half an hour with 7½ amperes, no chlorate was produced, and in this apparatus the electrolysis of potassium iodide was considerably less than in the other one.

Measurements of the molecular elevations produced have been made with a number of electrolytes and non-electrolytes, and the results obtained are given in the following tables. Where possible our results have been compared with those obtained by other observers at approximately the same concentration of solution.

In column A the strength of the solution in gram-molecules per litre is given. The figures in column B represent the observed rises in temperature, whilst those in column C show the molecular elevation of the boiling point calculated from A and B. In the remaining columns the values for C obtained by other observers are given.

	A.	B.	C.	Kg.	W. Bz.	S.
Potassium chloride	0·2715	0·250	9·26	9·24	—	—
	0·736	0·672	9·17	9·18	9·33	9·03
	1·105	1·018	9·24	9·22	9·25	9·19

	A.	B.	C.	Kg.	W. Bz.	S.	H. Bz.
Sodium chloride ...	0·0564	0·059	10·8	—	—	10·5	10·8
	0·389	0·394	10·13	—	9·11	—	10·35
	0·442	0·439	9·94	9·14	9·51	9·3	10·35
	0·733	0·734	10·02	9·39	—	—	10·28
	1·390	1·440	10·38	10·13	9·67	10·04	10·56

	A.	B.	C.	F. Kr.
Sodium stearate	0·0330	0·026	7·90	—
	0·0867	0·026	3·00	1·85
	0·1354	0·015	1·11	1·12
Sodium palmitate	0·0486	0·018	3·75	7·92
	0·0961	0·028	2·92	4·42
	0·2227	0·045	1·98	2·24
	0·3705	0·063	1·70	1·63

	A.	B.	C.	L.	Bn.
Carbamide	0·0922	0·037	3·9	—	—
	0·317	0·134	4·22	—	4·32
	0·658	0·280	4·26	—	4·27
	0·989	0·444	4·52	4·74	4·35
	1·522	0·682	4·50	4·56	4·27

Satisfactory results were also obtained with potassium nitrate, sodium acetate, and sucrose.

Kg. = L. Kahlenberg (*J. Physical Chem.*, 1901, **5**, 366).

W. Bz. = W. Biltz (*Zeitsch. physikal. Chem.*, 1902, **39**, 414).

S. = A. Smits (*ibid.*, 1902, **40**, 208).

L. = W. Landsberger (*Zeitsch. anorg. Chem.*, 1898, **17**, 436).

Bn. = E. Beckmann (*Zeitsch. physikal. Chem.*, 1890, **6**, 459).

H. Bz. = H. Biltz ("Practical Methods for the Determination of Molecular Weights"; translated by Jones and King).

F. Kr. = F. Krafft (*Ber.*, 1895, **28**, 2573).

	A.	B.	C.
Potassium oxalate	0·190	0·228	12·0
	0·340	0·399	11·7
Sodium potassium tartrate	0·296	0·334	11·3
	0·729	0·820	11·3
	1·152	1·287	11·15
	1·615	1·732	10·75
	2·105	2·189	10·4
Picric acid	0·0960	0·081	8·45
	0·1025	0·097	9·45
	0·1185	0·110	9·30
Gallic acid	0·1980	0·099	5·00
	0·3960	0·179	4·65
	0·5940	0·267	4·50

The molecular weight of tannic acid in aqueous solution was found to be between 3000 and 4000.

We have used this apparatus in determining the molecular weights of some dyestuffs, including benzopurpurine and indigo-white. The results of these experiments are described elsewhere (*J. Soc. Dyers*, 1909, **25**, 194; 1910, **26**, 4).

It will thus be seen that by employing a heating coil of suitable resistance, internal electrical heating can be used for aqueous solutions. It possesses one great advantage over the usual method of heating in that absolutely constant readings are obtained without any special precautions. Where the necessary current and appliances are available, the electric heating is more convenient than gas heating.

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CXXVII.—*The Action of Sodium Methoxide on 2 : 3 : 4 : 5-Tetrachloropyridine. Part I.*

By WILLIAM JAMES SELL.

THAT halogen derivatives of pyridine, when heated with sodium methoxide, frequently yield hydroxy- instead of methoxy-compounds has been the usual experience of workers in this subject, but, so far, no satisfactory explanation of this reaction has been offered. In some recent experiments it was noticed that when the haloid pyridine derivative in question is gradually heated to 205° with excess of sodium methoxide in sealed tubes which had been partly exhausted before sealing, a quantity of gas was produced.

In order if possible to throw some light on the above reaction, it was determined to examine the nature of this gaseous product. Examination showed that the gas collected was mainly a mixture of methyl ether and hydrogen with a trace of methane.

The formation of ether and of hydrogen may possibly be thus formulated:

$$(a)\ RCl + CH_3{\cdot}ONa = NaCl + RO{\cdot}CH_3,$$
$$(b)\ RO{\cdot}CH_3 + CH_3{\cdot}ONa = RONa + (CH_3)_2O,$$

the solution when acidified giving the hydroxy-compound.

Further, it may be suggested that the following reaction would take place to some extent:

$$(c)\ RONa + CH_3{\cdot}OH = RO{\cdot}CH_3 + NaOH,$$

the sodium hydroxide thus formed giving, with the methyl alcohol, sodium formate and hydrogen, thus:

$$(d)\ NaOH + CH_3{\cdot}OH = H{\cdot}CO_2Na + 2H_2.$$

The latter is in accordance with some unpublished work, in which it is shown that in the action of sodium ethoxide on 2:6-dichloropyridine at 205° sodium acetate is produced in some quantity; the gas produced in this case, however, is composed mainly of ethylene and hydrogen. Further, no hydrogen is produced when a mixture of sodium ethoxide and ethyl alcohol is similarly treated.

EXPERIMENTAL.

The tubes were charged with 3 grams of tetrachloropyridine and about 40 c.c. of dry methyl alcohol in which 2 grams of sodium had been dissolved. The tubes were partly exhausted before sealing, and then gradually heated to 200—205° and maintained at that temperature for about four hours. When cold, the gas was collected in the usual manner. A preliminary trial was made with a tube charged as above, and the gas collected over water. At the moment of opening only a few c.c. of gas escaped from the previously partly exhausted tube, but on warming the tube to 30° a considerable volume collected in the jar. On leaving this overnight it was found that the greater part had dissolved in the water, and the residue consisted chiefly of hydrogen with traces of methane and a little nitrogen from the air left in the tube.

The gas from the other tubes was collected over mercury, and after being kept over calcium chloride to remove the vapour of methyl alcohol, a part was analysed with the following results:

Volume of gas taken	46·8 c.c.
After 1 c.c. sulphuric acid,	6·8 ,,
Further 0·40 c.c. sulphuric acid	6·8 ,,
After fuming sulphuric acid	6·8 ,,
Volume to eudiometer	6·8 ,,
,, + oxygen	13·3 ,,
After explosion	3·9 ,,
,, sodium hydroxide	3·5 ,,
,, pyrogallol	1·6 ,, =nitrogen.

Percentage Composition.

Methyl ether	85·48
Olefines	00·00
Hydrogen	12·24
Methane	00·85
Nitrogen	3·42
	101·99

A further experiment was made on a sample of the gas which had remained for twenty-four hours over calcium chloride. The volume of gas taken was roughly 200 c.c. It was syphoned into a nitrometer, and the supposed ether absorbed by 1·5 c.c. of sulphuric acid, the residual gas being rejected. The sulphuric acid solution of ether was diluted with a small amount of water, and the gas thus liberated was collected in a eudiometer and exploded with oxygen:

Volume of gas	2·9 c.c.
,, ,, + oxygen	19·2 ,,
,, after explosion	13·5 ,,
,, ,, KOH	7·7 ,,
,, ,, pyrogallol	0·0 ,,

These results show that we are here dealing with a gas which requires three times its own volume of oxygen for complete combustion, and gives twice its own volume of carbon dioxide. Eudiometrically, the possibilities are ethylene and methyl ether, but the former is practically ruled out by the general properties of the gas. Finally, the boiling point of the liquefied gas was determined. This was done by filling a wide tube of about 200 c.c. capacity, having a narrow tube sealed on to the top, bent twice at right angles, and sealed. The tube containing the gas was transferred to a tall mercury trough, and a stick of calcium chloride inserted and allowed to remain twenty-four hours. The free end of the narrow tube was then immersed in an air-jacketed bath of ethyl alcohol previously cooled to −50°. The gas liquefied, and formed about 0·5 c.c. of a clear, colourless liquid, which when the temperature of the bath was gradually allowed to rise, began to boil at −23°, and had disappeared at −21°. An experiment of a similar nature on methyl ether prepared in the usual way gave the boiling point −23° measured by the same thermometer.

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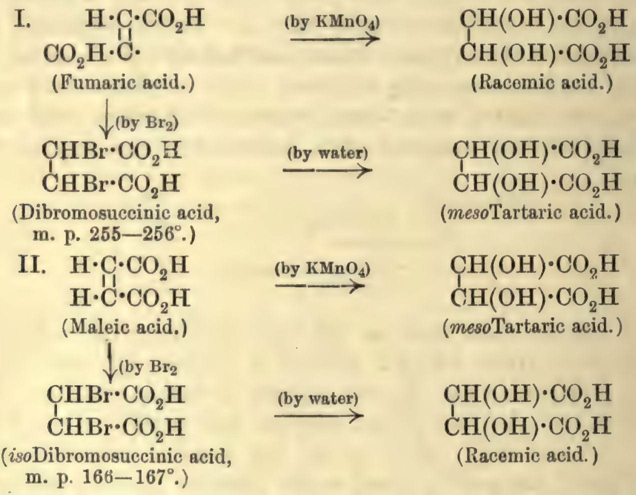
CXXVIII.—*Configuration of the Stereoisomeric Dibromosuccinic Acids.*

By ALEX. McKENZIE.

THE attention of the author was directed to the question of the configuration of the stereoisomeric dibromosuccinic acids in consequence of the following remarkable changes which are recorded in the literature:



I.

$$\begin{array}{c}\mathrm{H\cdot C\cdot CO_2H}\\ \|\\ \mathrm{CO_2H\cdot C\cdot}\end{array} \xrightarrow{\text{(by KMnO}_4\text{)}} \begin{array}{c}\mathrm{CH(OH)\cdot CO_2H}\\ |\\ \mathrm{CH(OH)\cdot CO_2H}\end{array}$$

(Fumaric acid.) (Racemic acid.)

$$\downarrow \text{(by Br}_2\text{)}$$

$$\begin{array}{c}\mathrm{CHBr\cdot CO_2H}\\ |\\ \mathrm{CHBr\cdot CO_2H}\end{array} \xrightarrow{\text{(by water)}} \begin{array}{c}\mathrm{CH(OH)\cdot CO_2H}\\ |\\ \mathrm{CH(OH)\cdot CO_2H}\end{array}$$

(Dibromosuccinic acid, m. p. 255—256°.) (*meso*Tartaric acid.)

II.

$$\begin{array}{c}\mathrm{H\cdot C\cdot CO_2H}\\ \|\\ \mathrm{H\cdot C\cdot CO_2H}\end{array} \xrightarrow{\text{(by KMnO}_4\text{)}} \begin{array}{c}\mathrm{CH(OH)\cdot CO_2H}\\ |\\ \mathrm{CH(OH)\cdot CO_2H}\end{array}$$

(Maleic acid.) (*meso*Tartaric acid.)

$$\downarrow \text{(by Br}_2$$

$$\begin{array}{c}\mathrm{CHBr\cdot CO_2H}\\ |\\ \mathrm{CHBr\cdot CO_2H}\end{array} \xrightarrow{\text{(by water)}} \begin{array}{c}\mathrm{CH(OH)\cdot CO_2H}\\ |\\ \mathrm{CH(OH)\cdot CO_2H}\end{array}$$

(*iso*Dibromosuccinic acid, m. p. 166—167°.) (Racemic acid.)

Fumaric acid behaves on oxidation in accordance with the conception of *cis*-addition so ably advocated by J. Wislicenus, the double linking being severed, and the hydroxy-groups taking up a position on the same side of the new molecule. Both Pasteur and Jungfleisch had, however, shown that a mixture of racemic and *meso*tartaric acids could be obtained when the silver salt of dibromosuccinic acid was acted on by water. Again, Kekulé boiled dibromosuccinic acid with water, and isolated calcium *meso*tartrate from the product of the reaction, a result which was also arrived at by Anschütz. On the other hand, whilst maleic acid underwent oxidation in accordance with the views of Wislicenus, racemic acid was obtained by Demuth and Victor Meyer from *iso*dibromosuccinic acid, and Kekulé remarked that the behaviour of the silver salt of this bromo-acid towards water was similar to that of the silver salt of the isomeric acid, inasmuch as a mixture of racemate and *meso*tartrate was formed. The conversions of dibromosuccinic acid into *meso*tartaric acid and of *iso*dibromosuccinic acid into racemic acid were inexplicable on the current views of addition to unsaturated compounds. As a consequence of the investigations, more particularly of Lossen and of Michael, these views have not stood the test of experiment; on the contrary, as pointed out by Frankland in his Presidential Address (this vol., p. 654), *trans*-addition to acetylenic or ethylenic compounds is the rule rather than the exception.

The action of water and of bases on the dibromo-acids under consideration was studied in detail by Lossen. When salts of the *iso*-acid were acted on by two equivalent amounts of base in aqueous solution, acetylenedicarboxylic acid was formed, both at the ordinary temperature and on boiling. The following three reactions took place when aqueous solutions of the acids were heated with water:

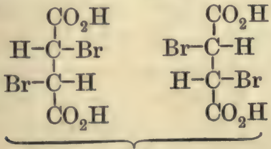
(1) $CO_2H\cdot CHBr\cdot CHBr\cdot CO_2H = HBr + CO_2H\cdot CBr{:}CH\cdot CO_2H.$

(2) $CO_2H\cdot CHBr\cdot CHBr\cdot CO_2H + H_2O = 2HBr + 2CO_2 + CH_3\cdot CHO.$

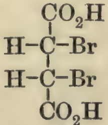
(3) $CO_2H\cdot CHBr\cdot CHBr\cdot CO_2H + 2H_2O = 2HBr + CO_2H\cdot CH(OH)\cdot CH(OH)\cdot CO_2H.$

A mixture of dihydroxy-acids was formed in each case, and consisted of about 75 per cent. of *meso*tartaric acid, when dibromosuccinic acid was decomposed, and of about 81 per cent. of racemic acid from *iso*dibromosuccinic acid.

In spite of the large amount of research devoted to the dibromosuccinic acids,* the question of their configuration had not been settled. Obviously one of them (I) must be resolvable into optically active components, and the other (II) must be of the *meso*-type:



(I.)



(II.)

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* For references to the literature, Meyer and Jacobson, *Lehrbuch der organischen Chemie*, 1910, Erster Band, Zweiter Teil, 524, may be consulted.

In the present paper it is shown that dibromosuccinic acid may now be designated as *meso*dibromosuccinic acid and *iso*dibromosuccinic acid as *r*-dibromosuccinic acid. The alkaloid employed for effecting the resolution of the latter acid was morphine, but special precautions had to be taken owing to the ease with which bromine was eliminated. *l*-Dibromosuccinic acid melts at 157—158°, and has $[\alpha]_D^{13}$ $-148°$ in ethyl acetate solution.

The conclusion that *iso*dibromosuccinic acid is resolvable into optically active components was arrived at independently by Holmberg (*Svensk Kem. Tidskr.*, No. 5, 1911), who was not aware of the author's preliminary note on this subject (Proc., 1911, **27**, 150). Holmberg's publication, which is also of a preliminary nature, appeared several months later than the author's, and describes the partial resolution of the acid by means of cinchonine, the difficulties encountered being similar to those of the author. The most active product obtained by Holmberg had $[\alpha]_D$ $-137{\cdot}6°$ in ethyl acetate solution, but he does not claim to have obtained the optically pure acid.

The transformations referred to at the beginning of this paper bear a close analogy to those involving a Walden inversion. In the displacement of halogen by the hydroxy-groups, it was conceivable that one had to deal with a change of configuration, or, in other words, with a process which was closely analogous to a Walden inversion.* The other alternative was that the direct hydroxylation of fumaric and maleic acids with permanganate followed a stereochemical course of a different order from that followed by the direct addition of bromine. The experiments of the author are in favour of the latter view. Further, since the oxidation of fumaric and maleic acids by permanganate does not apparently lead to the formation of a mixture of racemic and *meso*tartaric acids, it appears likely that the configurational change takes place during the addition of bromine. The problem encountered here is similar to that in a Walden inversion, for the proof of the occurrence of which phenomenon two different substitution processes are necessary, and it is difficult to say at which one of these the configuration is altered.

It was not found possible to prove that *l*-tartaric acid can be obtained from *l*-dibromosuccinic acid or its salts by the action of water, since, in addition to the formation of bromofumaric acid, profound racemisation took place. This is another example of the case where the halogen in direct attachment to an asymmetric carbon atom in an optically active acid is very readily removed by the action of water, the resulting hydroxy-acid being highly racemised [compare the action of water on *l*-phenylchloroacetic acid (McKenzie and Clough, Trans., 1908, **93**, 811; 1909, **95**, 777) and on *l*-α-chloro-α-phenylpropionic acid (Trans., 1910, **97**, 1016)].

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* I am in favour of restricting the term "Walden inversion" to changes undergone by optically active substances only. E. Fischer (*Annalen*, 1911, **386**, 374) attributes to me the extension of the term to configurational changes with optically inactive compounds, a view with which he does not agree. Perhaps the statement "a process which was equivalent to a Walden inversion with optically inactive material" in the preliminary note (*loc. cit.*) is liable to misconception.

A. McK.

EXPERIMENTAL.

Bromination of Maleic Acid.

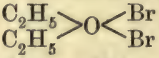
A mixture of dibromosuccinic acid (m. p. 255—256°) and *iso*dibromosuccinic acid (m. p. 166—167°) was obtained by Kekulé (*Annalen*, 1861, **117**, 123; *Annalen, Suppl.*, 1861, **1**, 131, 352, and 1862, **2**, 88) by the bromination of maleic acid in the presence of water, and the separation of these acids was effected by taking advantage of the readiness with which the *iso*-acid dissolves in water. Kekulé held the view that the *iso*-acid is derived from maleic acid, and that the concomitant formation of the isomeride is to be ascribed to secondary actions, namely, the transformation of maleic acid into fumaric acid by means of the hydrogen bromide evolved, and the subsequent bromination of the fumaric acid produced in this manner.

The experimental results of Kekulé were confirmed by Fittig and Petri (*Annalen*, 1879, **195**, 57), who further obtained no evidence for the formation of the *iso*-acid when fumaric acid was brominated. In the light of the observation of Fittig and Dorn (*Annalen*, 1877, **188**, 91) that maleic acid was readily converted into fumaric acid by fuming hydrogen bromide at the ordinary temperature, it accordingly appeared that maleic acid could be transformed into fumaric acid, both by bromine and by hydrogen bromide. Fittig and Petri did not, however, stop the bromination of maleic acid at the stage at which fumaric acid separated, but they prolonged the addition of bromine, since *iso*dibromosuccinic acid is separated more easily from its mixture with dibromosuccinic acid than from its mixture with fumaric acid.

The formation of fumaric acid by the bromination of maleic acid in the presence of water was also noted by Wislicenus (*Annalen*, 1888, **246**, 64), who recovered, as fumaric acid, no less than 27 per cent. of the original quantity of maleic acid.

The most practical method for preparing *iso*dibromosuccinic acid hitherto recorded is that of Michael (*J. pr. Chem.*, 1895, [ii], **52**, 293), who brominated a chloroform solution of maleic anhydride in the presence of sunlight, and decomposed the resulting *iso*dibromosuccinic anhydride with water.

The acid employed in the present research was prepared in the following manner: Bromine (19 c.c.) was gradually added within an interval of five minutes to 400 c.c. of ethyl ether (Kahlbaum's, dried over sodium). A slight elevation of temperature occurred. After ten minutes the clear liquid began to become turbid, and at this stage the addition of maleic acid (40 grams) was started, about 2 grams being added each time with constant shaking. The temperature of the ether was not allowed to rise above 25°. Towards the end of the action there was, as a rule, a very slight evolution of hydrogen bromide, but only the merest trace of fumaric acid was deposited. It is important that the preparation is conducted in dull daylight, and not in sunlight or in light rich in ultra-violet rays. The addition of maleic acid lasted about thirty minutes. The orange-coloured solution after being washed once with water, then with sulphurous acid, and finally twice with water, was dried over anhydrous magnesium sulphate. In order to minimise the risk of decomposition of the bromo-acid, the ether was allowed to evaporate spontaneously at the ordinary temperature, and the residual oily solid was dried in a vacuum over sulphuric acid for about a week until it became entirely solid. The yield varied from 75 to 91 grams. The *iso*dibromosuccinic acid obtained in this manner was free from fumaric and dibromosuccinic acids. It dissolved very readily in cold water, and melted and decomposed at 166—167°. (Found, Br = 57·8. Calc., Br = 57·9 per cent.; equivalent = 138·1. Calc., 137·9.)

Bromine combines with ethyl ether with great facility. This is shown clearly by Tschelinzeff and Konowaloff (*Ber.*, 1909, **42**, 1531), who ascribe the formula  $\frac{C_2H_5}{C_2H_5}\!>\!O\!<\!\frac{Br}{Br}$ to the additive compound produced by the interaction. This oxonium compound gradually separates as an oil when dry ether and bromine are mixed, and it doubtless acts in the foregoing preparation as a carrier of bromine. I find that whilst no obvious elimination of hydrogen bromide occurs during the separation of the oil, the latter decomposes very readily at the ordinary temperature with the evolution of hydrogen bromide and the formation of a compound (probably a brominated ether), which then undergoes further decomposition in the presence of water to give a mixture of ethyl bromide and an aldehyde.

Since the additive compound of bromine and ethyl ether separates much more readily in sunlight than in the dark, the maleic acid should accordingly be added in the preparation of *iso*dibromosuccinic acid before the separation of the oil commences, since the liberation of hydrogen bromide which so readily occurs from the oil is, of course, to be avoided.

In order to illustrate the effect of altering the conditions of the bromination of maleic acid in the presence of ether, the following experiments are perhaps worth recording. Maleic acid (100 grams) was added to 1 litre of commercial ether provided by a British firm. Bromine (44 c.c.) was then gradually added within an interval of thirty minutes in bright sunlight. The liquid quickly became turbid and warm, the maleic acid was gradually dissolved, hydrogen bromide was evolved, and a powdery solid separated in quantity. The mixture was cooled from time to time. The solid was separated and washed with ether; it amounted to 59 grams, and was identified as fumaric acid. (Found, equivalent = 58·0, the calculated value.) The ethereal solution contained the two isomeric dibromosuccinic acids with a large preponderance of the *iso*-acid.

When 200 c.c. of ethyl ether (Kahlbaum's, dried over sodium), 20 grams of maleic acid, and 9·2 c.c. of bromine were employed under conditions similar to the preceding, the yield of fumaric acid amounted to 3·1 grams, which is much less in proportion than before; the *iso*dibromosuccinic acid amounted in this case to 29 grams. The quality of the ether thus has an important influence.

Resolution of iso*Dibromosuccinic Acid.*

Several alkaloids were tried for the purpose of resolving the acid into its optically active components, and morphine was finally selected as the most suitable. The use of water as the solvent was at first attempted, the morphine being used in the proportion both of 1 mol. and of 2 mols. for 1 mol. of acid and the temperature conditions being varied. Water is, however, an impractical solvent. The *iso*-acid underwent a certain amount of decomposition into bromofumaric acid under the temperature conditions employed, and, owing to the ease with which hydrogen bromide was eliminated, the crystals which separated consisted mainly of morphine hydrobromide. A small proportion of lævorotatory *iso*-acid was actually obtained from these crystals, but the method obviously did not appear likely to be successful.

The solvent selected was methyl alcohol, and it was found advantageous to use equimolecular proportions of morphine and acid. The alkaloidal salt which separated when the *iso*-acid (1 mol.) was added to a solution of morphine (1 mol.) in methyl alcohol could not, however, be submitted to the customary treatment, namely, resolution by crystallisation. It was so very sparingly soluble, not only in methyl alcohol, but also in many other organic solvents, that crystallisation from such solvents was not a practical operation. It dissolved, however, in warm water, but the salt which separated was morphine hydrobromide. An acid of a high optical activity can, however, be obtained under the following conditions.

Morphine (21 grams, 1 mol.) was dissolved in warm methyl alcohol (290 c.c.), and, when the temperature of the solution was 46°, 19 grams (1 mol.) of the powdered *iso*-acid were added in one instalment, the mixture being shaken vigorously. The solution of the acid was immediately followed by the separation of glassy crystals of a morphine salt. After twenty-four hours at about 15°, the crystals (22 grams) were dissolved in dilute sulphuric acid. The acid obtained by extraction with ether amounted to 6·5 grams, and was strongly lævorotatory in ethyl acetate solution:

$$l=2,\ c=8{\cdot}6,\ \alpha_D\ -17{\cdot}32^\circ,\ [\alpha]_D\ -100{\cdot}7^\circ.^*$$

The mother liquor, from which the morphine salt had been removed, gave a dextrorotatory acid. 6·5 Grams of the acid with $[\alpha]_D$ −100·7° were then added to a solution of 7·1 grams of morphine in 100 c.c. of methyl alcohol. The resulting crystals (9·5 grams) gave an acid with the following rotation in ethyl acetate solution:

$$l=2,\ c=7{\cdot}4,\ \alpha_D\ -16{\cdot}93^\circ,\ [\alpha]_D\ -114{\cdot}4^\circ.$$

This acid (2·5 grams) was then acted on by a solution of 2·8 grams of morphine in 80 c.c. of methyl alcohol. The yield of salt was 3·5 grams, and the acid from this gave the following rotation in ethyl acetate solution:

$$l=2,\ c=8{\cdot}47,\ \alpha_D\ -19{\cdot}98^\circ,\ [\alpha]_D\ -118^\circ.$$

The acid was not yet homogeneous, and it was also obvious that the preparation of the optically pure acid could not be effected with readiness by this treatment.

Many unsuccessful attempts were made to obtain the pure *l*-acid by crystallising the strongly lævorotatory acid, which is easily obtained by treating the *iso*-acid once with morphine according to the method just described; for example, 25 grams of an acid with $[\alpha]_D$ −116° in ethyl acetate solution were crystallised first from benzene (1800 c.c.) and then from a mixture of benzene (200 c.c.) and acetone (6 c.c.), the acid being sparingly soluble in

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[*] The behaviour of the dibromosuccinic acid (m. p. 255—256°), obtained from fumaric acid, was examined under conditions similar to the above, 10 grams of acid, 12 grams of morphine, and 153 c.c. of methyl alcohol being used. The morphine salt did not separate at once as in the ease of the *iso*-acid, but, after five days, 4·5 grams had crystallised. The acid obtained from this salt was optically inactive. Other experiments on the action of various alkaloids on this dibromo-acid were made, and no evidence of the possibility of resolving it was obtained (compare Holmberg, *J. pr. Chem.*, 1911, [ii], **84**, 145).

boiling benzene and readily so in cold acetone. The product amounted to 8 grams, and had $[\alpha]_D$ −128° in ethyl acetate solution, but further attempts to obtain the pure acid by crystallising this product from boiling solvents failed owing partly to the tendency of the acid to decompose under the conditions employed.

The pure *l*-acid was finally obtained as follows: Morphine (83 grams) was dissolved by heating with methyl alcohol (1150 c.c.), and, when the temperature had sunk to 46°, *iso*dibromosuccinic acid (75 grams) was added. On shaking vigorously, the acid dissolved, and, two minutes after its addition, the morphine salt began to crystallise in glassy prisms. After eighteen hours at the laboratory temperature (summer), the crystals (87 grams) were removed.

Examination of Filtrate.—The filtrate was allowed to evaporate spontaneously. After a week, gritty crystals (8 grams), differing in appearance from those of the main quantity removed, had separated; they were sparingly soluble in dilute sulphuric acid, and they consisted of morphine hydrobromide. After several weeks the residual oily solid was decomposed by dilute sulphuric acid, and the bromo-acid extracted with ether. Thirty-four grams were obtained with the following rotation in ethyl acetate:

$$l=2,\ c=5{\cdot}45,\ \alpha_D\ +5{\cdot}07^\circ,\ [\alpha]_D\ +46{\cdot}5^\circ.$$

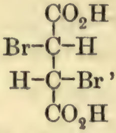
By adding a large excess of light petroleum to the concentrated solution of this product in ethyl acetate, a solid was obtained with $[\alpha]_D$ +7·7°. On allowing the solvent to evaporate at the ordinary temperature, and on repeating the treatment, a further solid with $[\alpha]_D$ +21·3° resulted, whilst the filtrate contained an oily dextrorotatory acid of high rotation. The separation of the pure *d*-acid from the latter product was not attempted.

Examination of Solid.—The 87 grams of morphine salt were decomposed by sulphuric acid, and the bromo-acid extracted with ether. The dried ethereal solution was allowed to evaporate spontaneously at the ordinary temperature in order to minimise the risk of decomposition. The resulting acid was at first oily, but ultimately became solid after ten days in a vacuum. Yield, 25 grams. On polarimetric examination in ethyl acetate solution it gave the value:

$$l=2,\ c=6{\cdot}99,\ \alpha_D\ -15{\cdot}57^\circ,\ [\alpha]_D\ -111{\cdot}4^\circ.$$

This product was very soluble in cold ethyl acetate. On dissolving a portion of it in the minimum amount of this solvent, and then adding a large excess of light petroleum or of carbon tetrachloride, the solid which separated was lævorotatory to a less degree than the original, whilst the acid obtained by allowing the filtrate to evaporate spontaneously at the ordinary temperature was more active; for example, when 5 grams of the acid were treated in this manner with light petroleum, 2·3 grams with $[\alpha]_D -82^\circ$ separated, whereas the acid obtained from the filtrate had $[\alpha]_D -128{\cdot}5^\circ$.

This tedious method was accordingly employed. The acid which separated was neglected, and the acid from the filtrate was examined polarimetrically, its concentrated solution in ethyl acetate then being precipitated afresh. At first light petroleum was used as the precipitant, and afterwards carbon tetrachloride. The acids obtained from the successive filtrates had the values $[\alpha]_D -127^\circ$, $-131{\cdot}6^\circ$, -140°, -144° under similar conditions of concentration in ethyl acetate. The acid with $[\alpha]_D -144^\circ$ was then crystallised twice from boiling benzene, in which it dissolved with great difficulty, the heating not being unduly prolonged. On cooling, the acid separated quickly in beautiful, glassy needles. After two more crystallisations from benzene, the rotation was practically unchanged. The yield of the pure acid was only about 1 gram.

l-*αβ-Dibromosuccinic acid*, 

$$\begin{array}{c}\mathrm{CO_2H}\\ |\\ \mathrm{Br{-}C{-}H}\\ |\\ \mathrm{H{-}C{-}Br}\\ |\\ \mathrm{CO_2H}\end{array}$$

, is very sparingly soluble in boiling benzene, from which it separates on cooling in glassy needles grouped in rosettes. It is easily soluble in ethyl acetate, acetone, methyl alcohol, or ethyl alcohol, and sparingly so in chloroform, light petroleum, or carbon tetrachloride. Like the *r*-isomeride, it dissolves very readily in cold water. It melts and decomposes fairly sharply at 157—158° with slight preliminary softening:

0·2013 required 28·1 c.c. of $N/19{\cdot}18$ baryta for neutralisation.
Equivalent = 137·4 (calc., 137·9).
0·2228 gave 0·3016 AgBr. Br = 57·6.
$C_4H_4O_4Br_2$ requires Br = 57·9 per cent.

Its specific rotation was determined in ethyl acetate solution:

$$l=2,\ c=5{\cdot}788,\ \alpha_D^{13} -17{\cdot}13^\circ,\ [\alpha]_D^{13} -148{\cdot}0^\circ.$$

The solution used in this determination was allowed to remain in the polarimeter tube for three days at the ordinary temperature; the rotation was then slightly greater than before, namely, $\alpha_D^{12} -17{\cdot}39^\circ$, whence $[\alpha]_D -150{\cdot}2^\circ$.

Action of Water on l-*Dibromosuccinic Acid and its Salts.*

The *l*-acid (0·2026 gram) was neutralised by $N/19{\cdot}18$ baryta, and evaporated on the water-bath to 8 c.c., the bulk necessary to fill a 2-dcm. tube. The solution was optically inactive.

The *l*-acid (0·2475 gram) was made up to 10 c.c. with water.

In a 2-dcm. tube fifteen minutes after the solid was dissolved the α_D was −3·08° ($t=12·5°$), whence $[\alpha]_D^{12·5}$ −62·2°. The solution was slowly evaporated to dryness during one hour, and the solid then dissolved in sufficient water to fill a 2-dcm. tube; the value α_D −0·36° was observed, but after heating for five hours at 100° this solution became optically inactive.

The decomposition of the *l*-acid by water takes place slowly at the ordinary temperature. 0·6408 Gram of a mixture of *l*- and *r*-acids with $[\alpha]_D$ −112° in ethyl acetate solution was made up to 10 c.c. with water; a portion of this solution was introduced into a 2-dcm. tube, and examined at intervals with the following result:

			α_D.
10th	February,	1911	−6·20° (initial value)
11th	,,	,,	6·13
14th	,,	,,	5·65
20th	,,	,,	4·61
28th	March	,,	1·62
1st	May	,,	0·64
30th	September	,,	0·03

An experiment on the action of water on a larger scale was accordingly made with a solution of 13·5 grams of acid (with $[\alpha]_D$ −100·7° in ethyl acetate) in 200 c.c. of water. After eight hours at 100° the solution was concentrated by evaporation to a bulk sufficient to fill a 2-dcm. tube, when a slight lævorotation was observed, namely, −0·15°; when neutralised by sodium hydroxide and again evaporated, the rotation was now dextrorotatory, namely, +0·25°. It is accordingly impossible to draw the conclusion that a small amount of *l*-tartaric acid is produced by the action of water on *l*-dibromosuccinic acid.

Silver *l*-dibromosuccinate (1·3 grams) was boiled with 50 c.c. of water for four hours, and the amount of hydrochloric acid requisite to precipitate all the silver in solution was added, the heating being continued for half an hour longer. The filtrate was evaporated to the bulk necessary to fill a 2-dcm. tube, and then gave α_D −0·09°.

A slight lævorotation was also observed with the product obtained by boiling 1·4 grams of an acid with $[\alpha]_D$ −129°, 4·7 grams of silver oxide, and 340 c.c. of water for ten hours. A little hydrochloric acid was added, and the filtrate when evaporated to small bulk gave α_D −0·08° in a 2-dcm. tube.

The author desires to express his thanks to the Government Grant Committee of the Royal Society for a grant in aid of this research.

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CXXIX.—N-*Chloro-derivatives of Benzylidene-diamides.*

By **Frederick Daniel Chattaway** and **Alan Edulf Swinton.**

The benzylidene-diamides which are produced when benzaldehyde is heated with amides, although very easily decomposed with regeneration of the aldehyde and amide, yield *N*-chloro-derivatives with hypochlorous acid. From benzylidenediacetamide the dichloro-compound has been prepared, but from benzylidenedibenzamide only the monochloro-derivative has been obtained, this, on account of its sparing solubility, being easily isolated. These compounds show the usual general characteristics of chloroamino-derivatives. They are easily hydrolysed, even on long exposure at the ordinary temperature to moist air, benzaldehyde and *N*-chloro-acetamide or -benzamide being formed.

They react vigorously with warm concentrated potassium hydroxide solution, benzaldehyde, potassium carbonate, and a primary amine being produced. Probably hydrolysis as above first takes place, the chloro-amide subsequently undergoing the Hofmann transformation under the influence of the alkali hydroxide.

There seems no reason whatever to assume that an alkyl *iso*cyanate is formed as an intermediate product in this and similar reactions, the normal course of which appears to be a Beckmann transformation, followed by progressive hydrolysis, thus:

$$\mathrm{R{\cdot}CO{\cdot}NHCl} \longrightarrow \mathrm{Cl{\cdot}CO{\cdot}NHR} \longrightarrow \mathrm{KO{\cdot}CO{\cdot}NHR} \longrightarrow \mathrm{CO(OK)_2 + NH_2R}.$$

Under suitable conditions an *iso*cyanate can be produced, thus:

$$\mathrm{Cl{\cdot}CO{\cdot}NHR} \longrightarrow \mathrm{HCl + CO{:}NR},$$

but its production is by no means a necessary step in the reactions which precede the amine formation.

N-*Lichlorobenzylidenediacetamide*, $C_6H_5{\cdot}CH(NCl{\cdot}CO{\cdot}CH_3)_2$.

Benzylidenediacetamide is best prepared by boiling for about ten minutes equivalent quantities of acetamide and benzaldehyde until water vapour ceases to be evolved. Longer heating considerably diminishes the yield. On cooling, the substance solidifies, and is easily purified by crystallisation from alcohol, from which it separates in long, hair-like crystals melting at 245° (Bülow, *Ber.*, 1893, **26**, 1974, gives 240—241°). The dichloro-derivative is prepared by suspending benzylidenediacetamide in chloroform, and shaking with excess of a saturated solution of bleaching powder acidified with acetic acid until a clear chloroform solution is obtained. On separating this and evaporating off the solvent at a low temperature, the dichloro-derivative is left as an oil, which solidifies after being kept for some hours in a desiccator. It can be recrystallised from a mixture of chloroform and petroleum, from which it separates in colourless, short prisms melting at 74—75°.

It was analysed by dissolving a weighed quantity in acetic acid, adding potassium iodide, and titrating the liberated iodine with standard thiosulphate:

0·3008 liberated I=43·6 c.c. *N*/10-I. Cl=25·69.

$C_{11}H_{12}O_2N_2Cl_2$ requires Cl=25·78 per cent.

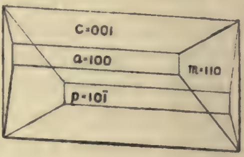
Dr. J. Drugman has examined the crystals, and describes them as follows:

Monoclinic: $a:b:c=2·163:1:3·041$; $\beta=106°56'$.

Forms observed: $c=(001)$, $a=(100)$, $m=(110)$, $n=(10\bar{1})$; prismatic ‖ the *b*-axis.

The measurements are only approximate, as the faces are rarely well developed.

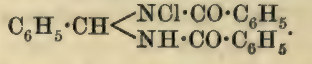
	Observed.	Calculated.
100—001	=73°04′	—
100—110	=64°12′	—
100—$10\bar{1}$	=41°20′	—
001—110	=82°54′	82°43′
110—$10\bar{1}$	=71°06′	70°54′
001—$\bar{1}01$	=65°45′	65°36′
110—$\bar{1}10$	=51°22′	51°36′



Cleavage ‖ (100); good. Optic axes in the plane of symmetry. One axis is visible on (001) towards acute edge a'/c; on (100) a bisectrix is seen towards the obtuse edge a/c, and an optic axis towards the acute edge a/c'.

N-*Dichlorobenzylidenediacetamide* reacts vigorously with alkali hydroxides. When a concentrated aqueous solution of potassium hydroxide is poured over the finely powdered solid, violent action accompanied by the evolution of much heat sets in. On distilling in a current of steam, a little benzaldehyde and methylamine are obtained. An odour recalling that of pyridine is noticeable during the distillation. The compound to which this is due, whatever its nature, is, however, formed in too small an amount for identification. On acidifying the alkaline residue after distillation, a quantity of benzoic acid separates.

N-*Chlorobenzylidenedibenzamide*,



$$C_6H_5\cdot CH<\begin{matrix}NCl\cdot CO\cdot C_6H_5\\ NH\cdot CO\cdot C_6H_5\end{matrix}.$$

Benzylidenedibenzamide is best obtained exactly as the diacetamide by heating a mixture of equivalent quantities of benzaldehyde and benzamide to boiling for five to ten minutes until water ceases to be evolved. The product, which is very sparingly soluble, is crystallised from alcohol, separating in silky needles melting at 228°.

On account of the sparing solubility of benzylidenedibenzamide in dilute acetic acid, the action of hypochlorous acid on it is so slow that if sufficiently prolonged to convert the compound into the dichloro-derivative so much hydrolysis occurs that little besides benzoic acid and nitrogen chloride is obtained. The monochloroderivative was obtained as follows: Five grams of benzylidenedibenzamide were dissolved in warm glacial acetic acid, and the solution was added to an excess of a solution of bleaching powder, so that the benzylidenedibenzamide was precipitated in a very fine state of division; 80 c.c. of chloroform were added, and the whole was vigorously shaken until the solid had nearly all dissolved. The chloroform solution was then separated, and well shaken with fresh bleaching powder solution slightly acidified with acetic acid. It was finally separated, dried, and the solvent evaporated. Chlorobenzylidenedibenzamide was left as a white solid, which was recrystallised from a mixture of chloroform and light petroleum.

N-*Chlorobenzylidenedibenzamide* crystallises from chloroform in rosettes of thin, needle-shaped crystals melting at 117°, and decomposing with evolution of gas at 140—150°. It was analysed as described above:

0·3072 liberated I=16·1 c.c. *N*/10-I. Cl=9·29.

$C_{21}H_{17}O_2N_2Cl$ requires Cl=9·72 per cent.

When heated with concentrated aqueous potassium hydroxide, a reaction similar to that with dichlorobenzylidenediacetamide occurs, but it is not at all violent, benzaldehyde, aniline, potassium carbonate, and benzamide being produced. Potassium hydroxide has, under similar conditions, little or no action on the benzylidenediamides.

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CXXX.—*The Absorption Spectra of Certain Aromatic Nitroamines and Nitroamides.*

By Gilbert T. Morgan, Edgar Jobling, B.Sc., and
Raymond T. F. Barnett, B.Sc.

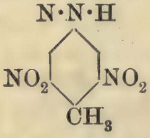
In a former communication a spectroscopic study of the nitration products of dimethyl-*p*-toluidine was described, the results of which showed that the character of the selective absorption of the dinitroamines derived from this base varied very remarkably with the orientation of the two nitro-substituents (Morgan and Clayton, Trans., 1911, **99**, 1945).

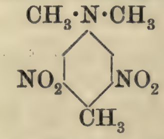
The absorption curves of 3:5- and 2:6-dinitrodimethyl-*p*-toluidine depart considerably from the form generally exhibited by aromatic nitroamines in the almost complete suppression of the characteristic absorption band. In these isomerides the two nitro-groups are symmetrically placed with regard to the amino-group, the former base having these radicles in ortho-positions, whereas in the latter the meta-positions are occupied. Similar curves with very flattened bands have been observed in the case of 3:5-dinitroaniline and 5-nitro-*m*-phenylenediamine (Hantzsch, *Ber.*, 1910, **43**, 1669). These four nitro-bases have one constitutional feature in common, namely, the symmetrical grouping of nitro- and amino-radicles, and accordingly it was presumed that the flattening of the absorption band was in some way connected with this symmetrical arrangement of the substituents.

The object of the present investigation was to test the validity of this hypothesis.

2:6-Dinitro-*p*-toluidine, prepared by Holleman and Böeseken's method (*Rec. trav. chim.*, 1897, **16**, 425) from 2:4:6-trinitrotoluene, was crystallised repeatedly from 40 per cent. acetic acid. In Fig. 1 (lower half) the absorption curve of this base is compared with that of 2:6-dimethyl-*p*-toluidine (Morgan and Clayton, *loc. cit.*), and it will be seen that the primary base shows a flattened band very similar to that of the tertiary amine, but with the head of the band a little more towards the blue end.*

The molecules of these two bases have the same degree of symmetry:





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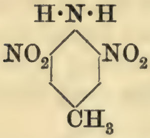
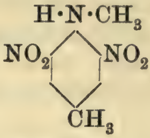
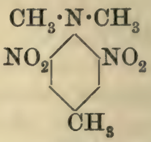
* Throughout this investigation, the absorption spectra were examined in absolute alcoholic solution; the source of light was an iron arc, and a quartz spectrograph of high dispersive power was employed.

both as regards the radicles associated with the aminic nitrogen and the orientation of the nitro-groups. These similarities also support the view that the symmetrical arrangement is in some way associated with the flattening of the absorption band.

Further attempts to illustrate this relationship showed, however, that it is not general, this fact being discovered by a comparative study of the absorption spectra of the following compounds:


(I.)


(II.)


(III.)

3 : 5-Dinitro-*p*-toluidine (I) and 3 : 5-dinitrodimethyl-*p*-toluidine (III) have the same degree of symmetry; their two nitro-groups are in ortho-positions with respect to aminic nitrogen, and this atom is associated with the same 3 : 5-dinitro-*p*-tolyl group and either two hydrogen atoms or two methyl groups. 3 : 5-Dinitromethyl-*p*-toluidine (II) is less symmetrical than the other two bases, for although its nitro-groups are similarly situated, its aminic nitrogen atom is associated with three different radicles (hydrogen, methyl, and 3 : 5-dinitro-*p*-tolyl).

If, therefore, the character of the selective absorption of these compounds is due mainly to the symmetrical arrangement of their substituent radicles, the primary and tertiary bases should certainly give similarly modified absorption curves, whereas that of the secondary amine might or might not differ from these, depending on the effect produced by the dissymmetry of the basic group.

An examination of 3-nitro-*p*-toluidine and the corresponding methyl and dimethyl derivatives by Baly, Tuck, and Marsden (Trans., 1910, **97**, 581) showed that, in this set of bases, successive methylation of the primary amine had no very marked effect on the shape of the absorption curve, the head of the band being only slightly shifted towards the red.

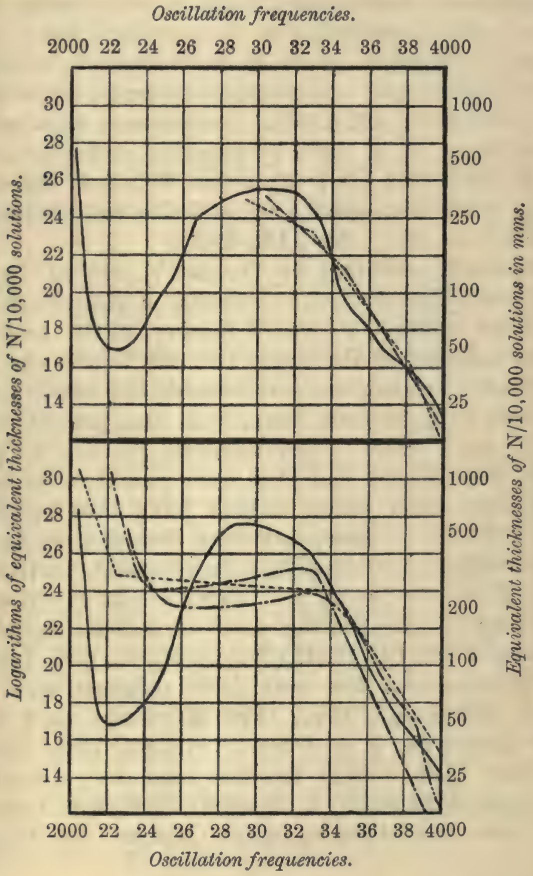
If this result were general, one would expect the three dinitro-compounds now under consideration to give very similar absorption curves. The comparison is shown in Fig. 1. 3 : 5-Dinitro-*p*-toluidine (m. p. 165—166°), prepared from 3 : 5-dinitroaceto-*p*-toluidide (*Annalen*, 1871, **158**, 341) and crystallised repeatedly from benzene and from carbon disulphide, gave an absorption curve of the normal form with a very persistent band (head 1/λ 2250 approx.). The absorption curve for 3 : 5-dinitromethyl-*p*-toluidine (m. p. 129°) was very similar to that obtained with the primary base, with a less persistent band shifted towards the red.

The absorption curve of 3:5-dinitrodimethyl-*p*-toluidine already given in the former communication (Morgan and Clayton, *loc. cit.*)

FIG. 1.

Upper curves.

Full curve : ———— 3 : 5-*Dinitromethyl*-p-*toluidine.*
Dotted curve : - - - - - - - - 3 : 5-*Dinitro*-p-*tolylmethylnitrosoamine.*
Dot and dash curve : — - — - — 3 : 5-*Dinitro*-p-*tolylmethylnitroamine.*



Lower curves.

Full curve : ———— 3 : 5-*Dinitro*-p-*toluidine.*
Dash and two dots curve : — - - — - - — 2 : 6-*Dinitro*-p-*toluidine.*
Dotted curve : - - - - - - - - - - - 3 : 5-*Dinitro*-p-*dimethyltoluidine.*
Dot and dash curve : — - — - — - 2 : 6-*Dinitro*-p-*dimethyltoluidine.*

was again plotted from a fresh photograph. The comparison shows that the curve of the tertiary amine with its band reduced to a step-out is quite unlike the curves obtained with the primary and secondary bases. From this example it is evident that symmetrical grouping of the nitro-substituents is not invariably accompanied by suppression of the absorption band.

*Nitration of Methyl-*p*-toluidine.*

Thomsen, who first studied methyl-*p*-toluidine, nitrated the base dissolved in glacial acetic acid (15 parts) with fuming nitric acid. A vigorous action occurred, and the solution, when poured into water, gave a crystalline mass of dinitromethyl-*p*-toluidine. The proportion of nitric acid and the temperature of nitration were not specified (*Ber.*, 1877, **10**, 1584). Gattermann obtained the same dinitro-compound (m. p. 129°) by nitrating methyl-*p*-toluidine with 5 parts of nitric acid (D 1·45) below 30°, and determined the orientation of the nitro-groups by oxidising the product to 3:5-dinitrobenzoic acid (*Ber.*, 1885, **18**, 1487).

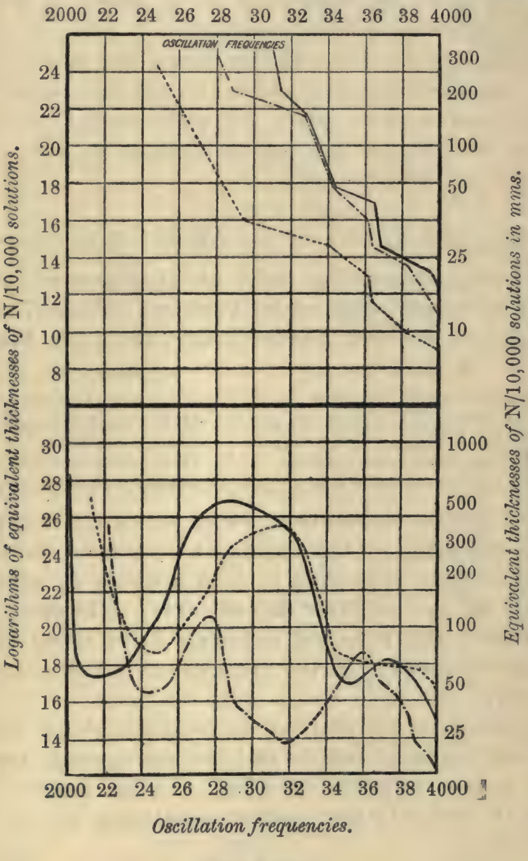
We proceeded according to Thomsen's method by dissolving 5 grams of methyl-*p*-toluidine in 75 grams of glacial acetic acid, and adding to the solution 10 c.c. of fuming nitric acid (D 1·50). During the addition of the nitric acid the liquid was maintained at the ordinary temperature. Afterwards the solution was heated on the water-bath for one hour, and then poured into a large volume of cold water. The nitration product (7 grams) was crystallised from alcohol and then from a mixture of benzene and light petroleum, pale yellow needles being thus obtained, which melted at 127—128°. Analysis showed that this substance was not 3:5-dinitromethyl-*p*-toluidine, but its nitroso-derivative. (Found, C=39·79; H=3·82; N=22·86. Calc., C=40·00; H=3·33; N=23·33 per cent.) The melting point of 3:5-dinitro-*p*-tolylmethylnitrosoamine, $NO\cdot N(CH_3)\cdot C_6H_2(NO_2)_2\cdot CH_3$, has been variously given at 125° (Gattermann, *loc. cit.*), 126° (Pinnow, *Ber.*, 1895, **28**, 3044; van Romburgh, *ibid.*, 1896, **29**, 1015), and recently as 127—128° (Reverdin, *J. pr. Chem.*, 1911, **83**, 168). The substance readily gives Liebermann's reaction, and its absorption curve (Fig. 1, upper dotted line) is identical with that of the substance prepared from dimethyl-*p*-toluidine (Morgan and Clayton, *ibid.*, p. 1903).

The final mother liquors from the nitrosoamine yielded bright red crystals soluble in cold concentrated hydrochloric acid, and on repeating the nitration at 10° with half the amount (5 c.c.) of nitric acid, this red substance became the main product. When crystallised from alcohol, the compound separated in bright red needles melting at 85°; it did not give Liebermann's reaction, and its absorption curve (Fig. 2, lower full line) shows the well marked band characteristic of 3-nitromethyl-*p*-toluidine (Baly, Tuck, and Marsden, *loc. cit.*). This base, which was formerly prepared by methylating 3-nitro-*p*-toluidine (Gattermann, *loc. cit.*), has thus been obtained as a direct nitration product of methyl-*p*-toluidine.

FIG. 2.

Upper curves.

Full curve : ———— *Toluene*-p-*sulphonyl*-1 : 6-*dinitro*-β-*naphthylamine.*
Dotted curve : - - - - - - - - *Toluene*-p-*sulphonylmethyl*-1-*nitro*-β-*naphthylamine.*
Dot and dash curve : — - — - — *Toluene*-p-*sulphonyl*-1-*nitro*-β-*naphthylamine.*



Lower curves.

Full curve : ———— 3-*Nitro*-p-*methyltoluidine.*
Dotted curve : - - - - - - - - o-*Nitroaniline.*
Dot and dash curve : — - — - — *Picramide.*

Preparation of 3:5-*Dinitromethyl*-p-*toluidine.*

Methyl-*p*-toluidine was nitrated in the foregoing manner to 3:5-dinitro-*p*-tolylmethylnitrosoamine, and this product oxidised to 3:5-dinitro-*p*-tolylmethylnitroamine (m. p. 138—139°) by heating gently for an hour with excess of fuming nitric acid (Reverdin, *loc. cit.*). The nitroamine, which was crystallised repeatedly from dilute alcohol, then contained $\mathrm{N}=21{\cdot}82$, theory requiring $\mathrm{N}=21{\cdot}88$ per cent.; it gave the absorption curve shown in Fig. 1 (upper half). The nitroamine was heated with 3 parts of phenol in a sealed tube at 170° for three to four hours, the product then added to dilute aqueous sodium hydroxide, and the precipitate crystallised repeatedly from alcohol, when 3:5-dinitromethyl-*p*-toluidine was obtained in well defined red needles melting at 129°. ($\mathrm{N}=20{\cdot}01$, theory requiring 19·91 per cent.)

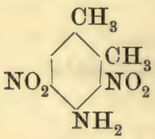
Absorption Spectra of the Dinitroamino-o-*xylenes.*

The following interesting series of dinitroamino-*o*-xylenes was kindly placed at our disposal by Professor Crossley, to whom we desire to express our best thanks (Trans., 1911, **99**, 2345):

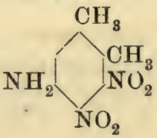
	Base.	Colour.	M. p.
1.	3 : 5-Dinitro-4-amino-*o*-xylene	Orange-red needles	143°
2.	3 : 4-Dinitro-5-amino-*o*-xylene	Deep orange-red needles	212
3.	4 : 5-Dinitro-3-amino-*o*-xylene	Orange needles	143
4.	5 : 6-Dinitro-3-amino-*o*-xylene	Deep yellow needles	172
5.	3 : 5-Dinitro-6-amino-*o*-xylene	Golden-yellow needles	161

The first three isomerides show broad persistent absorption bands of the type exhibited by the majority of aromatic nitroamines, the heads of the bands appearing in each instance at about $1/\lambda$ 2450 (Fig. 3, full curves and upper dotted curve). The second and third isomerides show also a second shallower band (head at $1/\lambda$ 3450) towards the violet end. In the first isomeride this band is reduced to a step-out.

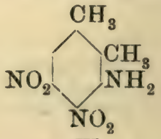
The graphic formulæ of these three dinitro-bases indicate that each contains the basic radicle and the nitro-groups arranged consecutively in the aromatic nucleus. In the second and third isomerides (V and VI) the relative orientation of these groups is



(IV.)



(V.)



(VI.)

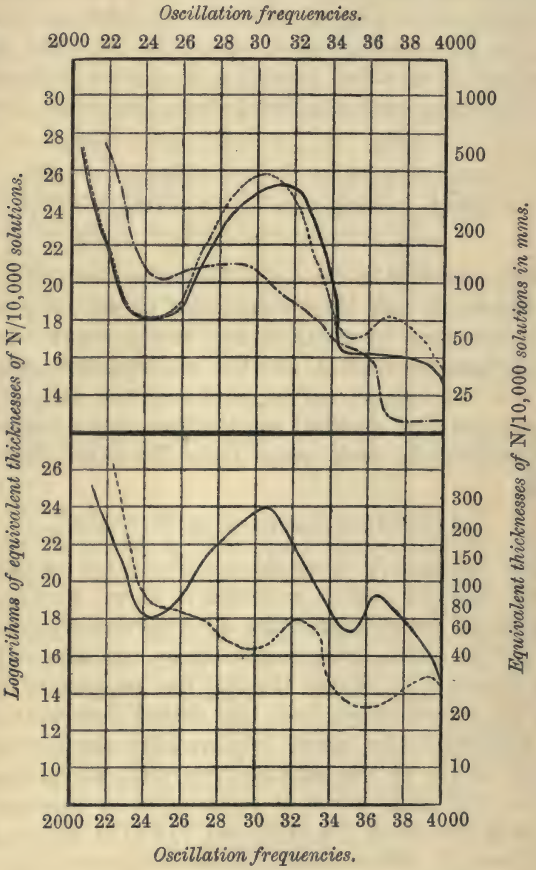
the same ($\mathrm{NH_2}:2\mathrm{NO_2}=1:2:3$), and in no case is a nitro-group in the para-position with respect to the amino-group.

The absorption spectra of the fourth and fifth isomerides show a very marked deviation from what may be termed the normal

FIG. 3.

Upper curves.

Full curve : ———— 3 : 5-*Dinitro*-4-*amino*-o-*xylene.*
Dotted curve : - - - - - - - - 3 : 4-*Dinitro*-5-*amino*-o-*xylene.*
Dot and dash curve : — - — - — 5 : 6-*Dinitro*-3-*amino*-o-*xylene.*



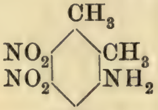
Lower curves.

Full curve : ———— 4 : 5-*Dinitro*-3-*amino*-o-*xylene.*
Dotted curve : - - - - - - - - 3 : 5-*Dinitro*-6-*amino*-o-*xylene.*

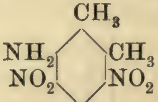
type of absorption exhibited by aromatic nitro-amines. The characteristic persistent band disappears, and in the fourth isomeride (VII) is represented by a very shallow band (head at 1/λ 2400), the second shallower band exhibited by the second and third isomerides being reduced to a step-out (1/λ 3400—1/λ 3600).

In the fifth isomeride the normal persistent band is replaced by a broad shallow band shifted towards the violet end (head at 1/λ 2950), and there is a second shallow band (head at 1/λ 3600) also more towards the violet than the narrower bands of the second and third isomerides.

The graphic formulæ (VII and VIII) for the fourth and fifth isomerides show that each of these dinitro-bases contains a nitro-group in the para-position with regard to the basic radicle, and to this extent they differ from the first three isomerides which contain only ortho- or meta-nitro-groups. In other respects it is scarcely likely that the fourth and fifth isomerides differ in chemical structure from the first three isomerides in any way that can be adequately indicated by modifications in the conventional graphic formulæ for these substances, and the spectroscopic anomalies indicated by their absorption curves emphasise the difficulty of correlating absorption and chemical constitution over a moderately wide range of compounds, even when these substances belong to the same class.



(VII.)



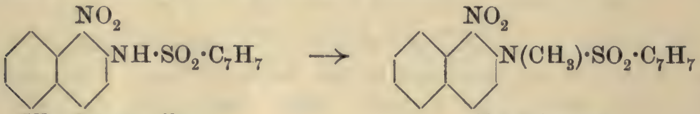
(VIII.)

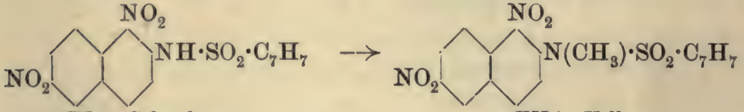
Absorption Spectrum of Picramide.

The effect on selective absorption produced by introducing three nitro-groups into the aniline molecule is shown by the absorption curve obtained from picramide (2:4:6-trinitroaniline, m. p. 187—188°), this curve being indicated by the dot and dash line on Fig. 2 (lower half), where the full line represents the curve of 3-nitrodimethyl-*p*-toluidine, and the dotted line that of *o*-nitroaniline. The two latter bases, employed for purposes of comparison, exhibit curves of the normal type with one persistent band, whereas the picramide curve is remarkable in showing two well-defined bands (heads at 1/λ 2450 and 1/λ 3150 approx.). In this respect picramide differs from all the polynitro-amines hitherto examined, including 2:3:6-trinitrodimethyl-*p*-toluidine (Morgan and Clayton, *loc. cit.*) and the *N*-substituted picramides studied by Hantzsch and Lister (*Ber.*, 1910, **43**, 1683, 1687).

*Absorption Spectra of the Nitration Products of Toluene-*p*-sulphonyl-β-naphthylamine and its Methyl Derivative.*

Toluene-*p*-sulphonyl-β-naphthylamine yields on nitration toluene-*p*-sulphonyl-1-nitro-β-naphthylamine (IX) and toluene-*p*-sulphonyl-1:6-dinitro-β-naphthylamine (XI); the former of these substances crystallises in orange-yellow prisms, and the latter in colourless, felted needles. When methylated, these compounds undergo a noteworthy colour change; the orange-yellow mononitro-derivative yields colourless toluene-*p*-sulphonylmethyl-1-nitro-β-naphthylamine (X), whereas the colourless dinitro-derivative furnishes yellow toluene-*p*-sulphonylmethyl-1 : 6-dinitro-β-naphthylamine (XII) (Morgan and Micklethwait, this vol., p. 148). The unmethylated compounds are strong acids, the imidic hydrogen in the group $C_7H_7\cdot SO_2\cdot NH$ being replaceable by metals (Na, Hg, Co, etc.), whereas the methyl derivatives are non-acidic:


(IX.) Orange-yellow. (X.) Colourless.


(XI.) Colourless. (XII.) Yellow.

These marked colour differences, coupled with the removal of acidic properties on alkylation, suggest a change in chemical constitution.

An examination of the absorption spectra of these compounds in alcoholic solution shows that they do not exhibit selective absorption, and that the general absorption observed can be indicated by curves (Fig. 2, upper half) of the same type, and having the form characteristic of the acyl derivatives of aromatic nitroamines (compare Fig 1, upper half).

Summary.

In this and the preceding communication (Morgan and Clayton, *loc. cit.*), eighteen aromatic nitroamines and six nitroamides have been examined spectroscopically.

(1) In the majority of cases the nitroamines show a well marked persistent band in the visible region, but in certain instances this band becomes considerably flattened, or even reduced to a step-out. This modification of the typical form was observed with certain

dinitrated primary and tertiary bases varying considerably among themselves in chemical configuration, so that at present it seems impossible to correlate the appearance of this spectroscopic anomaly with any definite change of chemical structure.

(2) The acylation of aromatic nitroamines with either inorganic acyl groups (NO or NO_2) or organic radicles, such as acetyl or toluene-*p*-sulphonyl, leads to the suppression of selective absorption; these acylated nitroamines show a general absorption, which is sometimes in the ultra-violet region, but not infrequently in the visible region. This observation corresponds with the general experience that acylation of an aromatic nitroamine leads to the production of either a colourless acyl derivative or at least of one which is less coloured than the parent base.

(3) Although in certain chemical respects picramide resembles the acid amides, yet it differs from the acylated nitroamines in exhibiting selective absorption with two well-marked bands.

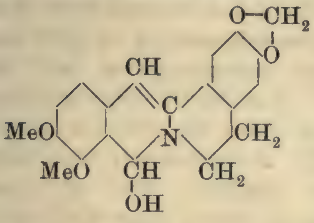
We desire to express our thanks to Professor Fowler for the use of his spectrograph, and to the Research Grant Committee of the Royal Society for a grant which has partly defrayed the expenses of this investigation.

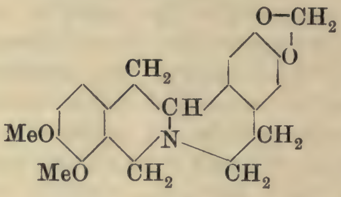
Royal College of Science, London.
South Kensington, S.W.

CXXXI.—*The Exhaustive Alkylation of Tetrahydroberberine.*

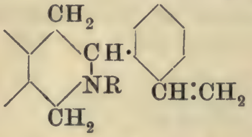
By James Wallace McDavid, William Henry Perkin, jun., and Robert Robinson.

Although analytical and synthetical methods have completely established the constitution of berberine (I) and most of its degradation products, there are still some problems connected with the constitution of this interesting alkaloid which have not been investigated, and since it is so readily available and its reactions always serve to shed valuable light on the structure of the rarer alkaloids, we have continued its investigation in the new direction described in this paper. This communication is an account of the exhaustive alkylation of tetrahydroberberine (II), a substance which, as is well known, results from the reduction of berberine (I) with acid reducing agents:

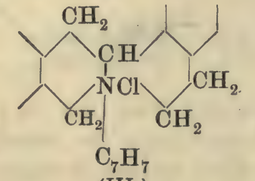

(I.)


(II.)

Tetrahydroberberine, containing as it does a system of fixed rings having a nitrogen atom common to two of them, requires a larger number of stages for the elimination of the nitrogen by exhaustive alkylation than any other base which has been investigated in this respect. The preparation of a methyltetrahydroberberine, or which, since it is actually derived from a base isomeric with tetrahydroberberine and containing the group:

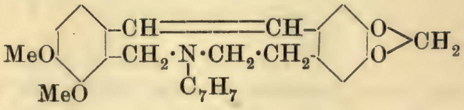

,

we prefer to call methyl*iso*tetrahydroberberine, has already been accomplished by Gaze (Beilstein's "Handbuch," III., 801, *Privatmitteilung*). This substance is produced from tetrahydroberberine by combination with methyl iodide and subsequent conversion into the methyl hydroxide, which, on heating in a stream of hydrogen at 100°, loses water and yields methyl*iso*tetrahydroberberine. We have endeavoured to improve this rather tedious process, but without success, and in consequence we experimented with benzyl chloride in the hope that the corresponding benzyl hydroxide would be less stable than the methyl hydroxide. Tetrahydroberberine benzyl chloride (III), produced by the action of benzyl chloride on tetrahydroberberine, is obtained in two modifications:

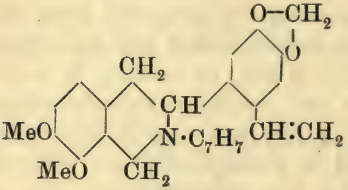

(III.)

which are doubtless stereoisomeric; the one (*a*) crystallising with two, and the other (*b*) with six molecules of water of crystallisation and melting at 197° and 87° respectively. That these hydrated substances are really different tetrahydroberberine benzyl chlorides is confirmed by the fact that, on complete dehydration over phosphoric oxide, they yield different substances, melting at 203° and 165° respectively. The possibility of stereoisomerism will be readily understood when we consider that, whilst tetrahydroberberine contains an asymmetric carbon atom, the addition of the benzyl chloride brings about asymmetry of the nitrogen atom also, so that *cis-trans*-isomerism becomes possible. One of these isomerides must, however, be exceedingly labile, since both yield one and the same substance containing one molecule of solvent on crystallisation from alcohol. A case which is probably of a similar type, namely, the existence of isomeric ethiodides of *d*- and *l*-canadine (*d*- and *l*-tetrahydroberberine), has already been observed by Gadamer and Voss (*Arch. Pharm.*, 1910, **248**, 43).

When either of the tetrahydroberberine benzyl chlorides is decomposed by means of alcoholic potassium hydroxide, an anhydro-base, *N*-benzyl*iso*tetrahydroberberine, is produced. This reaction might conceivably proceed in two directions, so as to yield substances of the constitutions (IV) and (V):

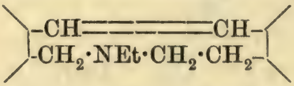


(IV.)

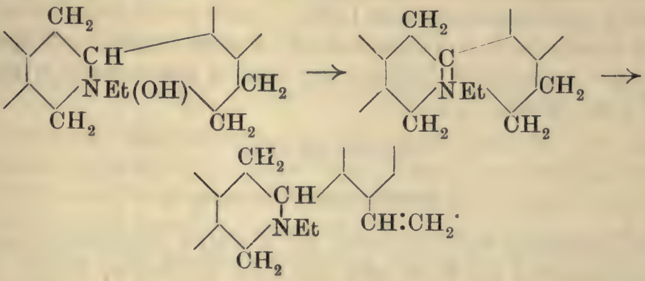


(V.)

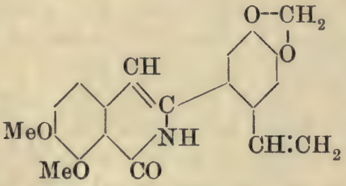
but formula (IV), containing as it does a ten-membered ring, seems improbable, and would not have been discussed were it not for the fact that a similar structure containing the group:



is proposed by Gadamer and Voss (*loc. cit.*) for the anhydro-base derived from tetrahydroberberine (or canadine) ethiodide. The argument employed by these authors in support of their contention is based on the production of an optically inactive anhydro-base from optically active canadine ethyl hydroxide by heat. This certainly indicates that the asymmetric carbon atom is concerned in the change, and the present authors suggest that the reactions involved are probably correctly represented in the scheme:



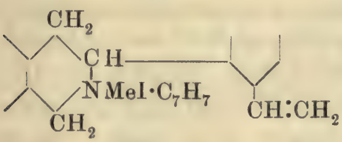
Formula (V) is analogous in structure to *iso*oxyberberine (VI):



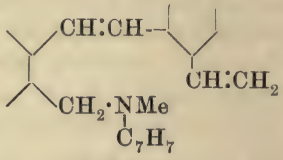
(VI.)

the formation of which from oxyberberine (Bland, Perkin, and Robinson, this vol., p. 262) involves a reaction similar to that which occurs in the production of the above anhydro-base.

N-Benzyl*iso*tetrahydroberberine yields a methiodide (VII) which with alcoholic potassium hydroxide is converted into a new anhydro-base (VIII), the structure of which does not necessarily depend on the adoption of (V) as the correct expression for *N*-benzyl*iso*tetrahydroberberine:

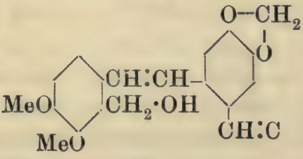


(VII.)



(VIII.)

The new base yields in its turn a methiodide which was converted into the methochloride and decomposed by boiling with concentrated aqueous potassium hydroxide followed by prolonged



(IX.)

distillation in a current of steam. Benzyldimethylamine was formed, together with a neutral substance, $C_{20}H_{20}O_5$, which evidently has the constitution (IX).

This substance is 3:4-dimethoxy-3′:4′-methylenedioxy-2-hydroxymethyl-6′-vinylstilbene, but for the sake of convenience it may be called *berberilene.*

EXPERIMENTAL.

Tetrahydroberberine.

This substance was prepared by a slight modification of the process described by Hlasiwetz and Gilm (*Annalen*, *Suppl.*, 1863, **2**, 192). Berberine sulphate (25 grams) dissolved in boiling water (500 c.c.) containing sulphuric acid (40 grams) and acetic acid (80 grams) was reduced by means of excess of zinc ribbon during several hours, and until the yellow colour of the solution had almost disappeared. After filtration, the solution was saturated with common salt, when tetrahydroberberine hydrochloride was precipitated as a pale yellow, amorphous solid. This was collected, dissolved in hot water, and decomposed with ammonia. The base was then purified by crystallisation from benzene, when prisms melting at 167° were obtained.

Tetrahydroberberine Methosulphate.—This derivative was prepared because it was thought that it might be more readily decomposed by alkali than the methiodide, which, however, is not the case.

Tetrahydroberberine (1 mol.) was dissolved in benzene and treated with pure methyl sulphate (1 mol.), when heat was developed and in a few seconds the additive compound crystallised. It was collected, washed with benzene, and recrystallised from ethyl alcohol, when colourless prisms melting at 224° were obtained:

0·1092 gave 0·2285 CO_2 and 0·0560 H_2O. C=56·8; H=5·7.

$C_{20}H_{21}O_4N(CH_3)_2SO_4$ requires C=56·8; H=5·8 per cent.

The substance is fairly readily soluble in hot water, from which it separates in large prisms containing solvent of crystallisation. When its solution in hot water was treated with a large excess of concentrated aqueous potassium hydroxide, no decomposition took place, since the salt crystallised unchanged from the solution, and after recrystallisation from alcohol the melting point was 224°:

0·1116 gave 0·2323 CO_2 and 0·0610 H_2O. C=56·8; H=6·1.

On boiling with alcoholic potassium hydroxide the salt was, however, decomposed, and tetrahydroberberine methyl hydroxide melting at 160—164° and identical with the substance prepared by Gaze (*loc. cit.*) was obtained. Since this substance requires to be heated at 100° in hydrogen to effect its decomposition into water and the anhydro-base, the process was abandoned in favour of a more convenient method.

The Tetrahydroberberine Benzyl Chlorides (a *and* b) (III, p. 1219).

In preparing these substances, tetrahydroberberine (30 grams) and benzyl chloride (12 grams) were heated at 100° for thirty hours. The resulting greyish-yellow solid was washed with ether and crystallised from water, when the salt separated in two distinct modifications; the first crop (*a*), when dried in the air, melted at 197°, and the second more soluble substance (*b*) melted at 87°. When these substances were recrystallised separately from water they did not undergo any change, and there can be little doubt that they are hydrated stereoisomeric tetrahydroberberine benzyl chlorides (compare p. 1220). As the following analyses clearly show, (*a*) has two, and (*b*) six molecules of water of crystallisation:

(*a*) 0·1229 gave 0·2892 CO_2 and 0·0708 H_2O. C = 64·2; H = 6·4.
0·1490 „ 0·3545 CO_2 „ 0·0877 H_2O. C = 64·9; H = 6·5.
0·3446 lost 0·0246 on exposure in a vacuum over P_2O_5. H_2O = 7·1.

$C_{27}H_{28}O_4NCl,2H_2O$ requires C = 64·6; H = 6·4; H_2O = 7·1 per cent.

(*b*) 0·1779 gave 0·3624 CO_2 and 0·1116 H_2O. C = 55·9; H = 7·0.
0·1460 „ 0·3024 CO_2 „ 0·0934 H_2O. C = 56·3; H = 7·1.
0·1563 „ 4·2 c.c. N_2 at 22° and 746·5 mm. N = 3·0.
0·3296 „ 8·6 c.c. N_2 „ 20° „ 726 mm. N = 3·0.
0·3772 „ 0·0965 AgCl. Cl = 6·3.
0·4365 lost 0·0750 in a vacuum over P_2O_5. H_2O = 17·2.

$C_{27}H_{28}O_4NCl,6H_2O$ requires C = 56·1; H = 7·0; N = 2·5; Cl = 6·2; H_2O = 17·1 per cent.

The anhydrous solid obtained by the dehydration of (*a*) melted at 203°, and on analysis:

0·1121 gave 0·2863 CO_2 and 0·0620 H_2O. C = 69·6; H = 6·1.
0·1123 „ 0·2837 CO_2 „ 0·0625 H_2O. C = 69·2; H = 6·1.

$C_{27}H_{28}O_4NCl$ requires C = 69·6; H = 6·0 per cent.

On the other hand, the anhydrous compound derived from (*b*) melted at 165°, and in this case the analytical result was not quite so sharp:

0·1095 gave 0·2753 CO_2 and 0·0599 H_2O. C = 68·5; H = 6·1.

On crystallisation from alcohol the original crude additive product, or the substances (*a*) or (*b*) yield colourless prisms melting at 200°. These were found to consist of tetrahydroberberine benzyl chloride with one molecule of ethyl alcohol of crystallisation. On analysis of air-dried specimens:

0·1064 gave 0·2671 CO_2 and 0·0645 H_2O. C=68·3; H=6·7.
0·1086 „ 0·2719 CO_2 „ 0·0665 H_2O. C=68·3; H=6·7.
0·1784 „ 0·0460 AgCl. Cl=6·4.
$C_{27}H_{28}O_4NCl,C_2H_6O$ requires C=68·0; H=6·6; Cl=6·8 per cent.

The presence of alcohol was confirmed by drying the substance at 50°, and distilling with water, when alcohol was recognised in the distillate by means of the iodoform reaction.

It is a very curious phenomenon that the two different substances (*a*) and (*b*) should yield the same compound after crystallisation from alcohol, and the high melting point would seem to indicate that the transformation is from (*b*) into (*a*).

N-*Benzyl*iso*tetrahydroberberine* (V, p. 1220).

Tetrahydroberberine benzyl chloride was found to be almost unchanged by aqueous potassium hydroxide, but its decomposition was readily effected in alcoholic solution.

Tetrahydroberberine benzyl chloride (20 grams) was dissolved in hot ethyl alcohol (100 grams), and boiled with an excess of solid potassium hydroxide for an hour on the steam-bath. After filtration, most of the alcohol was distilled off, when a brown, resinous solid (15 grams) separated from the residue. This could not be crystallised, but yielded a hydrochloride which separated from ethyl alcohol in colourless needles, and after drying at 120° melted at 214°. On analysis of a specimen dried at 120°:

0·1051 gave 0·2667 CO_2 and 0·0585 H_2O. C=69·2; H=6·2.
0·0847 „ 0·2160 CO_2 „ 0·0473 H_2O. C=69·4; H=6·2.
$C_{27}H_{28}O_4NCl$ requires C=69·6; H=6·0 per cent.

The Dibromide Hydrochloride.—In order to confirm the constitution assigned to this substance a few grams of the hydrochloride were dissolved in cold chloroform and treated with a 20 per cent. solution of bromine in chloroform, drop by drop, until the bromine was no longer absorbed. On allowing the solution to remain, pale yellow crystals melting at 195° separated, which consisted of the *dibromide* of N-*benzyl*iso*tetrahydroberberine hydrochloride*:

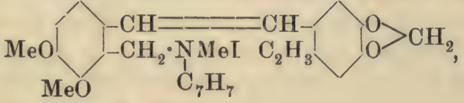
0·1069 gave 0·2655 CO_2 and 0·0466 H_2O. C=52·3; H=4·6.
$C_{27}H_{28}O_4NClBr_2$ requires C=51·8; H=4·5 per cent.

Methiodide.—This substance was easily prepared by boiling the base with an excess of pure methyl iodide for two hours, and the colourless solid which gradually separated from the clear solution was collected and crystallised from alcohol. This methiodide occurs in prisms melting at 187°:

0·1141 gave 0·2468 CO_2 and 0·0559 H_2O. C=57·0; H=5·4.
0·1130 „ 0·2462 CO_2 „ 0·0549 H_2O. C=59·4; H=5·4.
$C_{28}H_{30}O_4NI$ requires C=58·9; H=5·3 per cent.

In order to make quite sure that this compound is really the methiodide and not the hydriodide, the latter was prepared, and found to be quite a different substance. For this purpose *N*-benzyl*iso*tetrahydroberberine hydrochloride was treated in aqueous solution with potassium iodide; the precipitated salt was recrystallised from ethyl alcohol, when pale yellow crystals of the hydriodide melting at 197° were obtained.

Anhydro-N-*benzyl*iso*tetrahydroberberine Methyl Hydroxide Methiodide*, and the *Corresponding Methochloride.*



N-Benzyl*iso*tetrahydroberberine methiodide, like tetrahydroberberine methiodide, is not decomposed by aqueous alkali. When boiled with alcoholic potassium hydroxide it is, however, converted into a new amorphous base.

The methiodide (115 grams) was dissolved in alcohol (80 grams), and boiled with excess of powdered potassium hydroxide on the steam-bath for about an hour. The bulk of the alcohol was removed by distillation, and the solution cooled, when a yellow, semi-solid substance separated, which was several times washed with warm water and then dried. It became brittle on keeping, but all attempts to crystallise the substance or its salts failed. This base, which probably has the constitution assigned to it in the introduction (p. 1221), was therefore at once converted into its crystalline methiodide by boiling with an excess of methyl iodide during two hours. The colourless substance was recrystallised several times from methyl alcohol, from which it separates in transparent, well defined, rhombohedral plates melting at 191°. This methiodide is almost unaffected even by boiling alcoholic potassium hydroxide, and is only very slowly attacked by silver hydroxide. Since this behaviour is probably due to the sparing solubility of the substance in water, it was converted into the corresponding methochloride. For this purpose a paste of the methiodide and silver chloride with water was added to more water and boiled during two hours. The filtered solution contained no iodine, and, after concentrating and cooling, deposited a quantity of pale yellow plates which were recrystallised from acetone. The dry substance melts at 180°:

0·1096 gave 0·2825 CO_2 and 0·0693 H_2O. C=70·3; H=7·0.
0·1008 „ 0·2599 CO_2 „ 0·0622 H_2O. C=70·4; H=6·8.
$C_{29}H_{32}O_4NCl$ requires C=70·5; H=6·5 per cent.

This methochloride is gradually decomposed by silver hydroxide, but it was found to be more advantageous to employ a concentrated aqueous solution of potassium hydroxide as described in the next section.

3:4-*Dimethoxy*-3′:4′-*methylenedioxy*-2-*hydroxymethyl*-6′-*vinylstilbene* (*Berberilene*) (IX, p. 1221).

The methochloride (15 grams) described in the last section was dissolved in water, and a concentrated aqueous solution of potassium hydroxide added. A dark brown precipitate was soon formed, and the mixture was boiled and then subjected to steam distillation for fifteen hours at least. The aqueous distillate was acidified with hydrochloric acid, and evaporated nearly to dryness. Platinic chloride was then added, and the solution allowed to remain in the cold, when orange-yellow needles separated, and these after recrystallisation from water melted at 195°. (Found, Pt=28·7. $(C_7H_7NMe_2)_2H_2PtCl_6$ requires Pt=28·7 per cent.)

The base produced is therefore benzyldimethylamine. Under the above conditions, however, the decomposition was still incomplete, since the residue in the flask contained nitrogen. The solid residue was therefore washed with water to free it from potassium hydroxide, dried, and heated for eight hours at 130°. The product was collected and extracted with alcohol, dissolved in a small quantity of methyl ethyl ketone, and gradually precipitated by the addition of hot alcohol to the solution. The pale yellow powder so obtained commenced to decompose at 250°, and melted about 280°. It contained neither nitrogen nor halogen, and its analysis, combined with its method of preparation, is consistent only with the formula suggested:

0·1135 gave 0·2940 CO_2 and 0·0638 H_2O. C=70·6; H=6·2.
$C_{20}H_{20}O_5$ requires C=70·6; H=6·0 per cent.

Unfortunately, owing to the very small quantity of this substance available we have not yet been able to submit it to further investigation or to prepare derivatives.

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